ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIOENGINEERING

ENVIRONMENTAL ENGINEERING STREAM

CHROMIUM (III) REMOVAL FROM AQUEOUS SOLUTION USING MODIFIED *MORINGA OLEIFERA* SEEDPOD AS BIO-ADSORBENT

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A Thesis submitted to Addis Ababa University, Institute of Technology, School of Chemical and Bioengineering, in partial fulfillment for the requirements of Masters of Science in chemical engineering (Environmental Engineering).

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This is to certify that the thesis is prepared by Blen Tadesse, entitled: **Chromium (III) removal from aqueous solution using modified *Moringa oleifera* seedpod as bio-adsorbent** and submitted in partial fulfillment of the requirements for the Degree of Masters of Science in Environmental Engineering complies with the regulations of the University and meets the accepted standards with respect to originality and quality.

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I the undersigned declare that this **"chromium (III) removal from aqueous solution using modified *Moringa oleifera* seedpod as bio-adsorbent"** is my original work and has not been presented for any degree in any university and all the resource of materials used for this Thesis have been duly acknowledged.

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ABSTRACT

Tanning is the chemical process that converts animal hides and skin into leather and related products. The transformation of hides into leather is usually done by means of tanning agents and the process generates highly complex and characterized by high contents of organic, inorganic and nitrogenous compounds, chromium, sulfides, suspended solids and dissolved solids. This study deals with removal of chromium from tannery wastewater using modified Moringa oleifera seed pod (MMOSP) adsorbent. The collected MOSP crushed and sieved to a particle size between 125 and 250µm, Moringa oleifera seed pod was modified or treated with HNO_3 to remove metals and increase its surface area and after the acid treatment, the adsorbent was extracted with methanol to remove inorganic and organic matter from the sorbent surface. Finally washed with distilled water, dried at105^{o}c and characterized by FTIR and XRD. The adsorption efficiency MMOSP was evaluated as the function of adsorbent dosage, pH and contact time. Atomic absorption spectrometry (AAS) technique was used for the measurement of concentration of Cr (III) before and after adsorption. Batch adsorption experiments were conducted using model pollutant of tannery wastewater. The effects of independent variables on initial Cr (III) concentration of 150mg/L were evaluated. A Cr (III) removal efficiency of 99.78 % would be achieved at pH 5.5, 0.65g and 90min using modified Moringa oleifera seedpod. The experimental results have been fitted well by the Langmuir isotherm model with the higher correlation coefficients of R^2= 0.999. Thus, indicating to the applicability of monolayer coverage of the Cr (III) on the surface of the MMOSP. Adsorption kinetics was determined using pseudo first order and pseudo second order models and it was found that the adsorption process follows pseudo second order model (R^2=1). Generally, the results indicate that MMOSP may be used as a low cost adsorbent, alternative for treatment of effluents containing Cr (III).

***KEYWORDS**: Cr (III) Removal, modified Moringa olifera seed pod, adsorption isotherm model, and kinetics model*

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Table of content

LIST OF FIGURES

LIST OF TABLES

LIST OF ACRONYMS

MOSP	*Moringa oleifera* seedpod
MMOSP	Modified *Moringa oleifera* seedpod
EPA	Environmental Protection Authority
FTIR	Fourier Transform Infrared Spectrophotometer
XRD	X-Ray Diffraction
AAS	Atomic Adsorption Spectrometry
HNO_3	Nitric acid
Na (OH)	Sodium Hydroxide
Cr (III)	Chromium (III)
Cr (VI)	Chromium (VI)
$Cr_2 (SO_4)_3$	Chromium sulphate
COD	Chemical oxygen demand
BOD	Biological oxygen demand
UNIDO	United Nations Industrial Development Organization
HCl	Hydrochloric acid

1. INTRODUCTION

1.1. Background

Tanning is the chemical process that converts animal hides and skin into leather and related products. The transformation of hides into leather is usually done by means of tanning agents and the process generates highly turbid, colored and foul smelling wastewater. The major components of the effluent include sulfide, chromium, volatile organic compounds, large quantities of solid waste, suspended solids like animal hair and trimmings. For every kilogram of hides processed, 30 liters of effluent is generated .The various components present in the effluent affect human beings, agriculture and livestock besides causing severe ailments to the tannery workers such as eye diseases, skin irritations, kidney failure and gastrointestinal problems (Midha and Dey, 2008). The untreated release of tannery effluents containing high COD, BOD levels, trivalent chromium, sulfides, sodium chloride, organics and other toxic ingredients, to the natural water bodies effect flora and fauna of the ecosystem and increases the health risk of human beings.

It is in the interest of tanneries to produce as much tanned leather as possible, to the lowest possible cost, avoiding paying added costs for the reduction of the effects of pollution, which will increase proportionally to the commercial success of the tannery, while it is unacceptable for the surrounding communities. Postponing the solution of this problem will bring serious problems to the management of the environment, up to the extreme consequence of the impossibility to live in the area (Favazzi, 2003)

In Ethiopia, also there is a concern on the waste of the tanneries. The industrial establishments huge potential of for sustained economic development of the country has been constrained for they were not designed and operated in sustainable manner ,most of tanneries do not have treatment facilities and environmental management systems, as a result they simply discharge their wastes into the environment; etc. Thus, are causing serious environmental and public health problems in particular in urban centers. It is obvious that the effect will further extend to rural areas as well (EPA, 2005).

Conventional chrome tanning in leather production produces spent liquors containing significant amounts of chromium and other polluting substances, both organic and inorganic. From the total chromium used for tanning, only 60% to 70% is utilized, while the rest 30 to 40% remains in the spent tanning liquor (Cassano et al., 2007). About 30 to 40% of from the total amount of chromium used for

tanning in leather production process and disposed on to nearby water bodies, Conventional chrome tanning results in wastewater containing as high as 1500−3000 ppm (parts per million) of chromium; however, the present day high-exhaust chrome tanning methods lead to a wastewater containing 500−1000 ppm of chromium. But, the discharge limits for trivalent chromium vary broadly ranging from 1 to 5 mg/L. (Aravindhan et al.,2004)

In order to combat this problem, the commonly used procedures for removing metal ions from dilute aqueous streams include chemical precipitation, ion exchange, reverse osmosis and solvent extraction (Rich et al., 1987). However, these techniques have certain disadvantages such as incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require disposal.

Adsorption process is effective, and able to remove various levels of soluble heavy metals in solution. In recent years, considerable attention has focused on the removal of heavy metals using bio sorbents derived from low-cost materials. Several bio sorbents such as peat, tea waste, coconut husk, sewage sludge and rice husk will use for the treatment of metals in aqueous solution (Jang et al., 2005).

In this study, modified *Moringa oleifera* seedpod, which has environmental benefits in terms of the use of solid waste from other research centers and can be easily adopted in low cost to remove chromium. In addition, the effect of various parameters such as solution pH, contact time and adsorbent doses with respect to the percentage of removal of chromium ions would evaluate.

1.2. Statement of the problem

Tanning industry involves chemical reactions and mechanical changes, which use a lot of water. It generates waste most of the time in developing countries, which discharged in to the rivers or other water areas and open field land areas. It could have adverse effect on the environment and human if it not properly managed due to the presence of dangerous chemical and elements such as chromium, sulfur, etc. (Favazzi, 2003).

Ethiopian Tanneries discharge their wastewater effluents inadequately treated or totally untreated, directly in to rivers, other water bodies, and land without considering the level of damage it may bring to the local community at large. Currently, there are 26 tannery industries in operation, a good number of tanneries in Ethiopia have primary and secondary treatment to manage their wastes, but they do not follow

the right procedure to treat the waste by applying proper dosages of chemical, good maintenance, and continuous monitoring and evaluation. There are about 12,500-m^3wastewater and 150 tones solid wastes generated per day from all tanneries (LIDI, 2013).This subsequently causes both surface and ground water pollution and soil contamination with the toxic chromium metal. In addition, there are many city farms near these rivers, which might create a possibility for contaminated (untreated) tannery wastewater to enter in to the food chain. Particularly Chromium is not biodegradable and tends to bio-accumulate in living organisms causing serious disease and disorders.

Therefore, now it is time to develop cost effective and efficient treatment technology, by using alternative low cost adsorbent and effective removal of heavy metal ions like chromium from tannery wastewater. Adsorbent materials derived from low-cost agricultural wastes like the *Moringa oleifera* seedpod (MOSP) can use for the effective removal of heavy metal ions like chromium from tannery wastewater streams. *Moringa olifera* seed pod was mainly found in southern and eastern part of Ethiopia. The *Moringa oleifera* seed pod was obtained as a waste from bioflocculant (another study by different institutions).However, there is a minimal utilization of *Moringa oleifera* seed pods in water treatment as they are simply considered as agricultural wastes. Thus, investigating the suitability of *Moringa oleifera* seed pod as low cost alternative and effective adsorbent for the removal of chromium (III) from tannery wastewater.

1.3. Objectives of the study

1.3.1 General objective

The main objective of this study was to investigate chromium removal from aqueous solution using modified *Moringa oleifera* seed pod as bio-adsorbent.

1.3.2. Specific objectives

- To characterizes the *Moringa oleifera* seedpod.
- To investigate the effect of selected process variables (pH, time, and adsorbent dosages) on the adsorption performance of modified *Moringa oleifera* seedpod.
- To determine removal efficiency of the adsorbent
- To study the equilibrium adsorption isotherm and kinetics of chromium (III) ion adsorption by the adsorbent (*Moringa oleifera* seed pod)

1.4. Significance of the research

Tannery industry is well known one of the most polluting and hazardous manufacturing sector due to generating excessive solid, liquid and gaseous pollutants. Treating the tannery effluent contaminated with heavy metal with in the industrial premises before being discharge in to the environment is efficient way to remove heavy metals rather than treating high volumes of wastewater in a general sewage treatment plant. Therefore the significance of this study is reduction or removal one of the pollutants in tannery industry which is chromium (III),) ion discharged to environment from tannery industry effluent to meet effluent discharges concentration of the government regulation. Adsorbent such as activated carbon is one of the materials used in adsorption process, but it does not remove metal completely. Therefore, researches had studied to find other natural resources that could be an alternative to activated carbon. Several biomaterials such as tea waste, rice husk, coconut husk, oil palm fiber and *Moringa oleifera* seed pod are low cost agricultural residues and available in large quantities in southern Ethiopia. The utilization of natural and agriculture by-product as adsorbent not only economically feasible but instead of throwing away waste, it could be functional used as heavy metal ions adsorbent to reduce environmental pollution. Therefore, it is necessary to investigate and develop an adsorbent from *Moringa oleifera* seedpod because of its availability and capable removing Cr (III) from tannery wastewater.

2. LITERATURE REVIEW

2.1. Introduction

Environmental pollution, which arises from the development of modern industrial activities, is one of the most significant problems of the country. Most industrialists try to discharge their wastewater effluents inadequately treated or totally untreated, directly to rivers or nearby water bodies, and land without considering the level of damage it may bring to local community. Different industries discharge their wastes containing different heavy metals into the environment such as mining; energy and fuel production; electroplating; atomic energy installation and Leather manufacturing industry, etc. The most important technologies for removing metal ions from aqueous solution mainly consist of physical, chemical and biological technologies, which include chemical precipitation, ion exchange, membrane separation, coagulation-flocculation, and adsorption. Adsorption is a well-established and powerful technique for treating the industrial effluents. In comparison with conventional technology methods adsorption process, appeared to be preferable in terms of its efficiency, simplicity of design/operation, and the ease with which it can be applied in its application in the removal of heavy metals in wastewater (Frank, 2003).

2.2. Process flow of Tanning industry

In primitive times, man used animal skins to cover himself in order to protect him from the environment. Although skins were resistant and available, they had some weaknesses: they were damp, they would decompose and when trying to avoid purification by drying they lost their mechanical properties such as flexibility and softness due to drying. Because of this, leather production became an important craft dated more than 3000 years old. This process of turning skin into leather product is called tanning.

Tanning is a process where putrefaction is avoided while maintaining or enhancing the mechanical properties of being flexible and soft even when dry. Hides and skins gain durability and can be used in a wider range of products because of this process. These skins usually come from large and medium size mammals such as the ox, cow, calf, buffalo, sheep, goat, pig and horses; although marine animals and some reptiles are also processed. Leather processing is a technology that is composed of a series of step Operations that aim at isolating collagen by removing non-collage nous components of skin and then improving the material by making it more resistant to environmental and use factors (Favazzi, 2003).

Processing hides ad skins to convert them into leather has evolved through the years from a manual craft process into chemical intensive industrial process. According to (sharphouse, 1983), it is composed of the following three main stages:-

1. Pre-tanning (also known as beam house operations): this consists of unit operations from skinning the animal and preparing the skin for transport by curing, to treating the skin prior to tanning (washing, liming treatment, unhearing, fleshing, de liming, bating and pickling).

2. Tanning. (Also known as tannery operations): Tanning through chemical or vegetable treatment of the skin.

3. Post-tanning (finishing operations): That consists of operations to obtain the finishing mechanical and esthetic characteristics usually containing steps such as splitting to gain uniformed thickness, washing residue form tanning process, pH neutralizing, dyeing, flattening, oiling, drying and rolling. These steps require many natural resources such as water, metals, and derived chemicals in order to achieve the desired quality. If better manufacturing practices and control systems are not in place the tanning process can become an important environmental issue. Because of its potential and the many companies that have poor manufacturing practices, the tanning industry has generally been identified as a source of pollution and described as a problematic industrial sector in terms of environmental performance.

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By-products should be either reused/recycled or converted into new, higher value Products (DGEI, 2012)

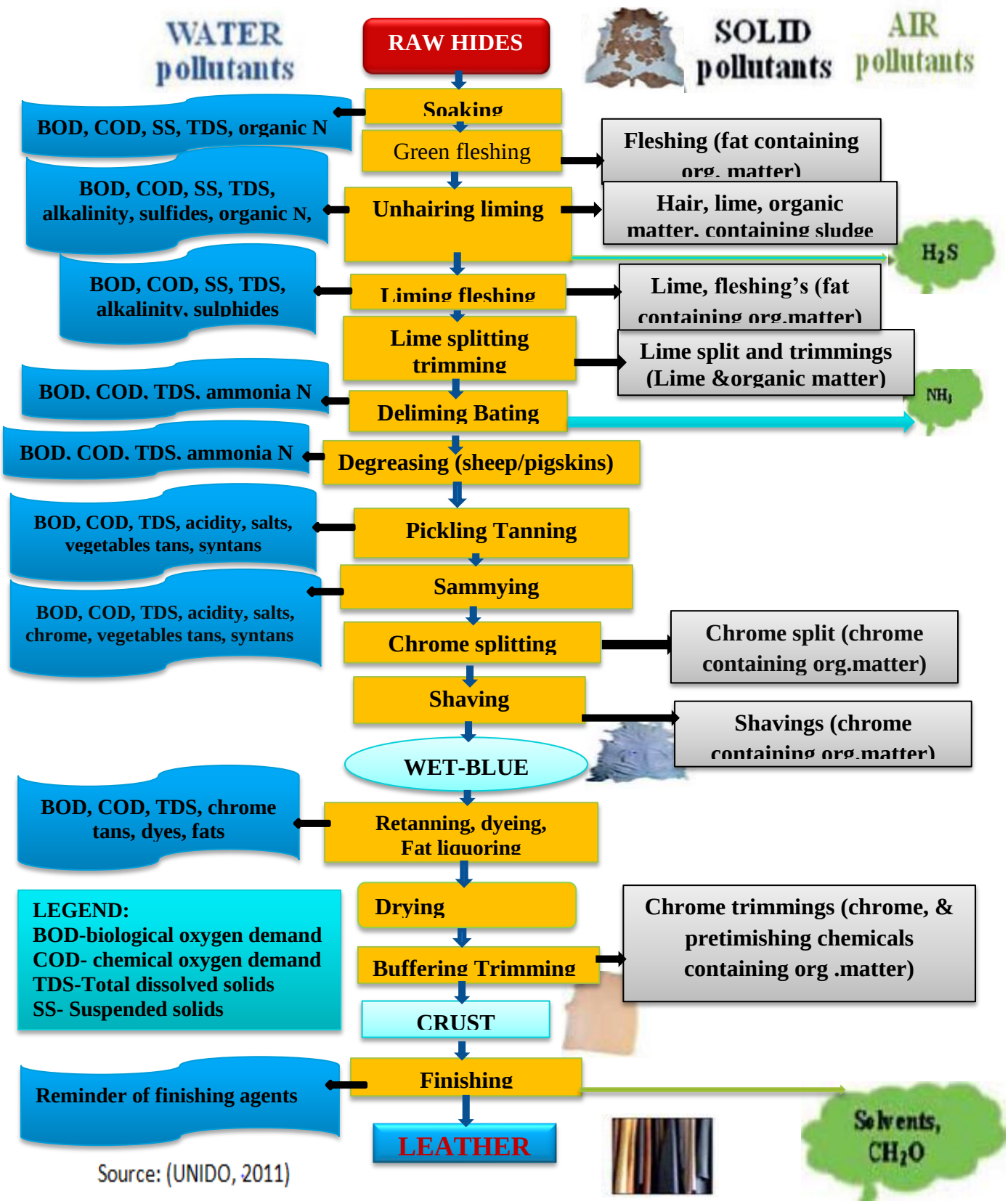

Figure 2.1:-schematic of tanning process starting from raw hides and skins to finished leather.

2.2.1. Pollution load of tanning industry

Due to variations in raw material, process, chemicals, water consumption, etc. it is small wonder that figures about pollution load in the literature vary a lot and should be interpreted very cautiously. The tables below and the chart on overleaf may give a general idea, the usual reference being one tone of wet-salted hides. (UNIDO, 2011)

Table 2.1: An example of average total pollution load – concentration in combined raw effluent, Conventional process, water consumption: 45m^3/ton.

Parameter	**Unit**	**Average total Pollution load**	**Typical limits, Surface waters**
BOD_5	mgO_2/L	2,000	30-40
COD	mg O_2/L	4,000	125-250
Suspended Solids(SS)	mg/L	2,000	35-100
Cr^{3+}	mg Cr/L	150	1.5-2.0
S^{2-}	mg S/L	160	1.0-2.0
Total nitrogen(TKN)	mg N/L	160	100
Cl^-	mg Cl/L	5,000	Locally specific
SO_4^{2-}	$mgSO_4/L$	1,400	Locally specific
Oil and grease	mg/L	130	Locally specific
TDS*	mg/L	10,000	Locally specific
PH		6-9	5.5-9.5

2.2. General description of chromium in environment

Chromium (Cr) is a naturally occurring element present in the earth's crust, with variableoxidation states. The most common oxidation states of chromium are 0, +2, +3 and +6 with +3 being the most stable. But only three oxidation states are found in nature; these are: Cr(0) which occur in metallic form, Cr(III) in chromic compounds and Cr(VI) occurs as soluble chromate(CrO_4^{2-})and dichromate ($Cr_2O_7^{2-}$) compounds (Jacobs and Testa,2005).

Chrome $^{3+}$ ***(chrome III)***

Chromium is mainly found in waste from the chrome tanning process; it occurs as part of the retaining system and is displaced from leathers during retaining and dyeing processes. This chrome is discharged from processes in soluble form; however, when mixed with tannery waste waters from other processes (especially if proteins are present), the reaction is very rapid. Precipitates are formed, mainly protein-chrome, which add to sludge generation. If chrome discharges are excessive, the chromium might remain in the solution. Even in low concentrations, it has a toxic effect upon daphnia, thus disrupting the food chain for fish life and possibly inhibiting photosynthesis.

Chrome^{6+} (hexavalent chrome, chrome VI)

Tannery effluents are unlikely to contain chromium in this form. Dichromates are toxic to fish life since they swiftly penetrate cell walls. They are mainly absorbed through the gills and the effect is accumulative.

2.2.1. Chromium Toxicity and its Accumulation

Industrial activities like electro plating, metal cleaning and dyeing processing, cement, and leather tanning are the major sectors that play role in releasing chromium into the environment. Chrome in the hexavalent form is very toxic. It is quite intriguing that contaminated field by industrial effluent show a mobilization ration of less than 5 (potentially toxic) for selected plant specious. Surprisingly, the mobilization ratios for weeds become greater than 5, which have healthy morphology in the early flowering stage (Kisku et al.,1999). A study done by (Marchese *et al.*,2008) about the rate of accumulation of chromium in four fresh water plant species, clams, crabs, and fishes showed that, all the four fresh water species and animals were found with high concentration of chromium which is an indication of its high accumulation potential. This clearly indicates that this problem become more serious and toxic to human beings, which are found at the top of the food web due to its toxicity and bioaccumulation effect.

In the tanning industry leather, processing involves conversion of put rescible hide or skin into leather. Tanning agents could help permanent stabilization of the skin matrix against biodegradation. This industry has gained a negative image in society with respect to its pollution potential and therefore is facing a severe challenge. The unit processes that cause tanneries the most difficult with regard to perceived environmental impact are unhearing and chrome tanning. Basic chromium sulfate (BCS) is a

tanning agent, which is employed by 90% of the tanning industry. Conventional chrome tanning results in wastewater containing as high as 1500−3000 ppm (parts per million) of chromium; however, the present day high-exhaust chrome tanning methods lead to a wastewater containing 500−1000 ppm of chromium (Aravindhan,2004). But, the discharge limits for trivalent chromium vary broadly ranging from 1 to 5 mg/L in the case of direct discharge into water bodies and 1 to 20 mg/L in the case of discharge into the public sewer system. Therefore, the treatment plant used by the tanning industry needs to treat the influent by 200 fold to send to water bodies, which is not practical in most of the cases (Tadesse et al., 2006).

Table 2.2: Chromium Toxicity Effects on Human Organs

Symptoms	**Affected organs**
Prolonged exposure to Cr^{+6} causes ulcers. Skin irritation is reported with prolonged exposure to Cr^{+3}. Dieses namely allergic dermatitis. Perforation of nasal septum occurs after exposure to Cr^{+6} or chromite dust.	• Skin
Air borne Cr^{+6}causes corrosion of bronco-pulmonary tract, irritation of mucous membrane, lung cancer.	• Nose • Lung • Lung
Tubular necrosis, renal insufficiency	• Kidney
Necrosis	• Liver
Damage	• Brain
Hyperchlorhydria	• Gastrointestinal Tract
Chromosomal aberrahos	• Mutagenicity

Source: (Sujana et al., 1997)

2.2.2. Chemical Properties of Chromium

Chromium is a fairly active metal. It does not react with water but reacts with most acids. It combines with oxygen at room temperature to form chromium oxide (Cr_2O_3). Chromium oxide forms a thin layer

on the surface of the metal, protecting it from further corrosion or rusting. The solubility of chromium compounds varies, depending primarily on the oxidation state. Trivalent chromium compounds, with the exception of acetate, hex hydrate of chloride, and nitrate salts, are generally insoluble in water. The zinc and lead salts of chromic acid are practically insoluble in cold water. The hexavalent chromium compounds are reduced to the trivalent form in the presence of oxidizable organic matter (Portier, 2012).

2.3. Overview of *Moringa oleifera*

The Moringaceae or Horseradish tree is the family of trees that consist of 13 different species, of which Moringaoleifera is the most widely cultivated. Moringa is native to the sub- Himalayan parts of Northern India, Pakistan, Bangladesh and Afghanistan (Oyeyinka, 2016). M.oleifera is a multi-purpose food plant, which originated, produced and used in many African countries, South America and New Zealand. However, it has been cultivated in many parts of the world and can now be found in almost all tropical countries (Hegde, 2015).*M. oleifera* typically grows in semi-dry, desert or tropical soils. Almost all parts of this plant: root, bark, gum, leaf, fruit (pods), flowers, seed and seed oil have been used for treating various ailments (Kesharwaniet al., 2014)

Water purification

Powdered seed act as a natural flocculent, able to clarify even the most turbid water. Seed powder can be used as a quick and simple method for cleaning dirty water. The powder joins with the solids in the water and sinks to the bottom. This treatment also removes 80-90% of bacteria contained in water. Using Moringa to purify water replaces Chemicals such as aluminum sulphate, which are dangerous to people and the environment, and are expensive (Mohmood*et al*., 2010).

Moringa oleifera tree (drumstick tree) is a rapid growing deciduous shrub or small tree of about 13m tall and 35cm in diameter with an umbrella-shaped open cap (Anjorin, 2010). *Moringa oleifera* is the most widely distributed species of the Moringaceae family throughout the World (Reddy et al, 2010). It has also been reported that *Moringa oleifera* oil and micronutrients contain antitumor, antiepileptic, antidiuretic, anti-inflammatory and venomous bite characters (Hsu, 2006). *Moringa oleifera* contains specific plant pigments with demonstrated powerful anti-oxidative ability such as vitamins C, E, A, caffe-oylquinic acids, carotenoids-lutein, alpha-carotene and beta carotene, kaempferol, quercetin, rutin (Siddhuraju ,2003).

Phytochemistry

Phytochemicals are, in the strictest sense of the word, chemicals produced by plants. Commonly, though, the word refers to only those chemicals, which may have an impact on health, or on flavor, texture, smell, or color of the plants, but are not required by humans as essential nutrients. An examination of the phytochemicals of *Moringa* species affords the opportunity to examine a range of unique compounds. In particular, this plant family is rich in compounds containing the simple sugar, rhamnose, and it is rich in a unique group of compounds called glucosinolates and isothiocyanates (Bennett et al., 2003; Fahey et al., 2001). For example, specific components of *Moringa* preparations that have been reported to have hypo tensive, anticancer, and antibacterial activity include4-(4'-O-acetyl-α-L rhamnopyranosyloxy)benzylisothiocy-anate[1],4-(α-L rhamnopyranosyloxy) benzyl isothiocy-anate[2], niazimicin[3], pterygospermin[4], benzyl isothiocyanate[5], and 4-(α-L rhamnopyranosyloxy) benzyl glucosinolate[6]. While these compounds are relatively unique to the *Moringa* family, it is also rich in a number of vitamins and minerals as well as other more commonly recognized phytochemicals such as the carotenoids (including β-carotene or pro-vitamin A). These attributes are all discussedextensively by (Lowell Fuglie, 1999) and others, and will be the subject of a future review in thisseries.

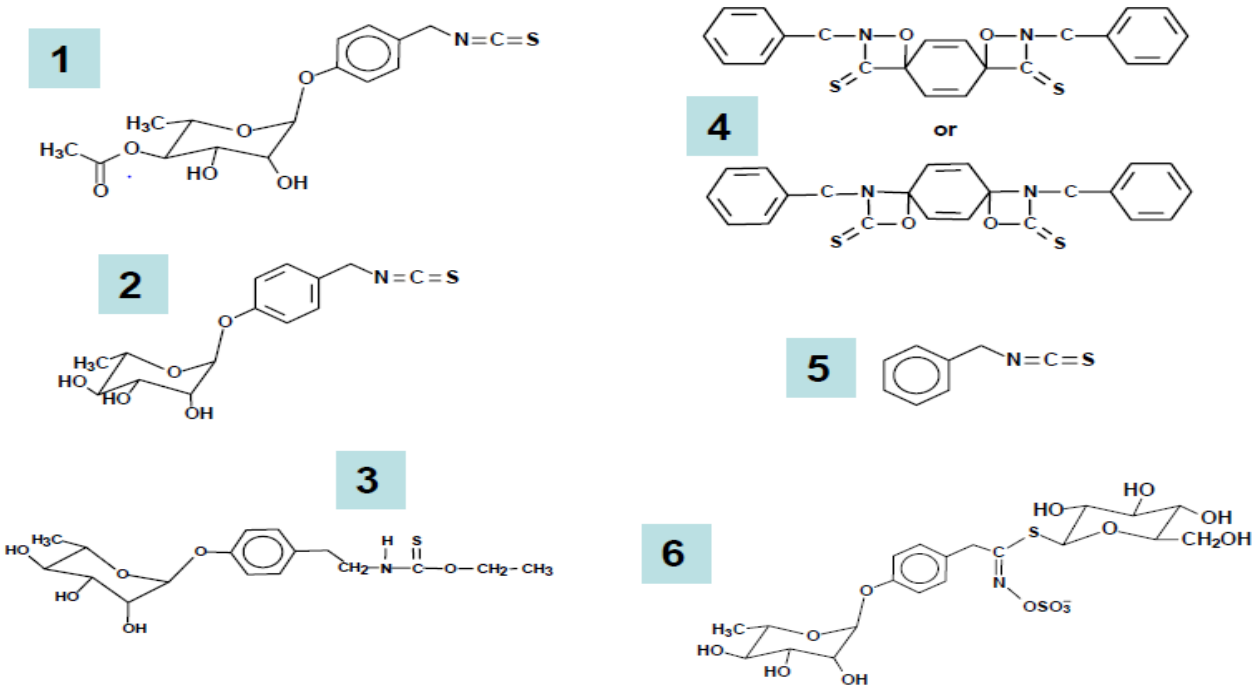

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Figure 2.2**:** Structures of selected phytochemicals from Moringa spp.

2.4. Conventional technologies for heavy metal removal

Heavy metal removal processes are carefully considered as not only toxic heavy metal removal in environmental aspects, but also precious metal recovery in industrial aspects. Chromium contamination is common all over the world. For water resources, the impact of this contamination is severe. Consequently, it is desirable to remove chromium from the contaminated water. Many treatment processes have been developed to remove chromium from wastewater. The most important of these technologies include; chemical precipitation, filtration, ion-exchange, electrolysis, lime coagulation, solvent extraction, reverse osmosis and electrocoagulation. However, all these technologies have their inherent advantages and limitations in application. Most of the methods suffer from some drawbacks such as incomplete metal removal, low selectivity, high reagent and energy requirement, high capital and operational cost and generation of toxic sludge or other waste product that require careful disposal has made it imperative for a cost effective treatment method.

2.4.1. Chemical Precipitation

Chemical precipitation is the method, in which dissolved and suspended Cr (VI) ions are transformed to the insoluble solid through a chemical reaction. Usually a precipitating agent accelerates this conversion from Cr (VI) ions into insoluble solid. The commonly used precipitation agents are lime and magnesia. This technique has been proven as an effective way to remediate chromium from wastewater. It is a simple, inexpensive, convenient, and safe method. However, this technique requires large amounts of chemicals, and excessive toxic sludge is produced. Sludge filtration and disposal increase the overall cost of the process. Sometimes Cr (VI) precipitation is slow, and aggregation of metal precipitates take place (Hyder et al., 2013).

2.4.2. Ion exchange

Ion exchange can attract soluble ions from the liquid phase to the solid phase, which is the most widely used method in water treatment industry. However, it requires pretreatment process to reduce suspended solids concentration in solution to prevent fouling or channeling. Ion exchange resins, either synthetic or natural solid resin, has the specific ability to exchange its cation with the metals in the wastewater. The most common cation exchangers are strongly acidic resins with sulfonic groups ($-SO_3H$) and weakly

acids resins with carboxylic acid groups (-COOH). Ion exchange resins have also been frequently used for the removal of chromium ions from aqueous solutions (Ahmad, 2014).

2.4.3. Reverse osmosis

The reverse osmosis process depends upon a semi-permeable membrane through which pressurized water is forced. Reverse osmosis, simply stated, is the opposite of the Natural osmosis process of water. Osmosis is the name for the tendency of water to migrate from a weaker saline solution to a stronger saline solution, gradually equalizing the saline composition of each solution when a semi-permeable membrane separates the two solutions. In reverse osmosis, water is forced to move from a stronger saline Solution to a weaker solution, again through a semi-permeable membrane. Because molecules of salt are physically larger than water molecules, the membrane blocks the Passage of salt particles (Barakat, 2011). The result is desalinated water on one side of the membrane and a highly concentrated, saline solution of water on the other side. The disadvantage of this method is that it is expensive (Ahalya *et al.*, 2003).

2.4.4. Coagulation -flocculation

Coagulation process is the destabilization of colloids by neutralizing the forces that keep them apart and reduces the net surface charge of the colloidal particles to stabilize by electrostatic repulsion process. Flocculation process continually increases the particle size to discrete particles through additional collisions and interaction with inorganic polymers formed by organic polymers added. Production of sludge, use chemicals and transfer of toxic compounds into solid phase are main drawbacks of the process. The objective of the coagulation depends on the source of water and the nature of the suspended, colloidal, and dissolved organic constituents (Crittenden, 2012).

2.4.5. Electro dialysis

Electro dialysis (ED) is a membrane separation in which ionized species in the solution are passed through an ion exchange membrane by applying an electric potential. The membranes are thin sheets of plastic materials with either anionic or cationic characteristics. When a solution containing ionic species passes through the cell compartments, the anions migrate toward the anode and the cat-ions toward the cathode, crossing the anion exchange and cat-ion exchange membranes (Chen, 2004). The disadvantage is the formation of metal hydroxides, which clog the membrane. In the electro-dialysis process, ionic

components of a solution are separated through the use of semipermeable ion-selective membranes. This process may be operated in either a continuous or a batch mode. Problems associated with the electro-dialysis process for wastewater renovation include chemical precipitation of Salts with low solubility on the membrane surface. To reduce the membrane fouling, Activated carbon pre-treatment, possibly preceded by chemical precipitation and some form of multimedia filtration may be necessary(Malkoc and Nuhoglu, 2005) .

2.4.6. Heavy metal removal using bio sorption

The conventional heavy metal removal processes have several disadvantages such as less effective removal of metal ion, high reagent requirement, high costs, the generation of toxic sludge's, and the problem of the safe disposal of the materials. Compared with conventional methods for removal of toxic heavy metals, bio sorption process offers the advantages of low cost, minimization of the volume of chemical and biological sludge to be disposed of, high efficiency in detoxifying very dilute effluents, and high metal selectivity. The advantages of bio sorption are cost effective, metal selective, regenerative, minimization of sludge generation, metal recovery, and competitive performance.

2.4.7. Adsorption

Adsorption is now recognized as an effective and economic method for heavy metal wastewater Adsorption is a surface phenomenon and is defined as the increase in concentration of a particular component at the surface or interface between two phases. Compound (pollutant) that sticks or adheres to the solid surface is called adsorb ate and the solid surface is known as an adsorbent adsorption is affected by temperature, the nature of adsorb ate and adsorbent, the presence of other pollutants and atmospheric and experimental conditions like pH, concentration of pollutants, contact time and particle size of the adsorbent. Bio sorption of heavy metals from aqueous solutions is a relatively new process that has been confirmed a very promising process in the removal of heavy metal contaminants. The major advantages of bio sorption are its high effectiveness in reducing the heavy metal ions and the use of inexpensive bio sorbents. Bio sorption processes are particularly suitable to treat dilute heavy metal wastewater (Fenglian and Wang, 2011)

The presence of suspended particles, oils, and greases reduces the efficiency of the process and, therefore, pre-filtration is sometimes required. When a finely divided solid is shaken with the

contaminated or polluted water, the pollutants adhere to the solid surface and a stage of equilibrium is established. At this stage, the concentration of pollutant adsorbed and in the water become constant. The relationship, at a given temperature, between the equilibrium amounts of pollutant adsorbed and in the water is called an adsorption isotherm. Langmuir, Freundlich and other models are well known and can explain the adsorption efficiency of a pollutant systematically and scientifically (Imran, 2007).

2.4.7.1. Adsorption mechanism

The classical mechanism of adsorption is divided into three steps Figure (2.3) a) diffusion of adsorbate to adsorbent surface, b) migration into pores of adsorbent c) monolayer build-up of adsorbate on the adsorbent. Figure (2.3) presents the process ofadsorbatedistribu-tion. The first stepoccurs diffusion of adsorbate on the adsorbent surface by intermolecular forces between adsorbate and adsorbent. The second step involves migration of adsorb-ate into pores of adsorbent. tributed on the surface and filled up the volume of pores, particles of adsorbate are building up the monolayer of reacted molecules, ions and atoms to the active sites of adsorbent. (Iakovleva and Sillanpää,2013).

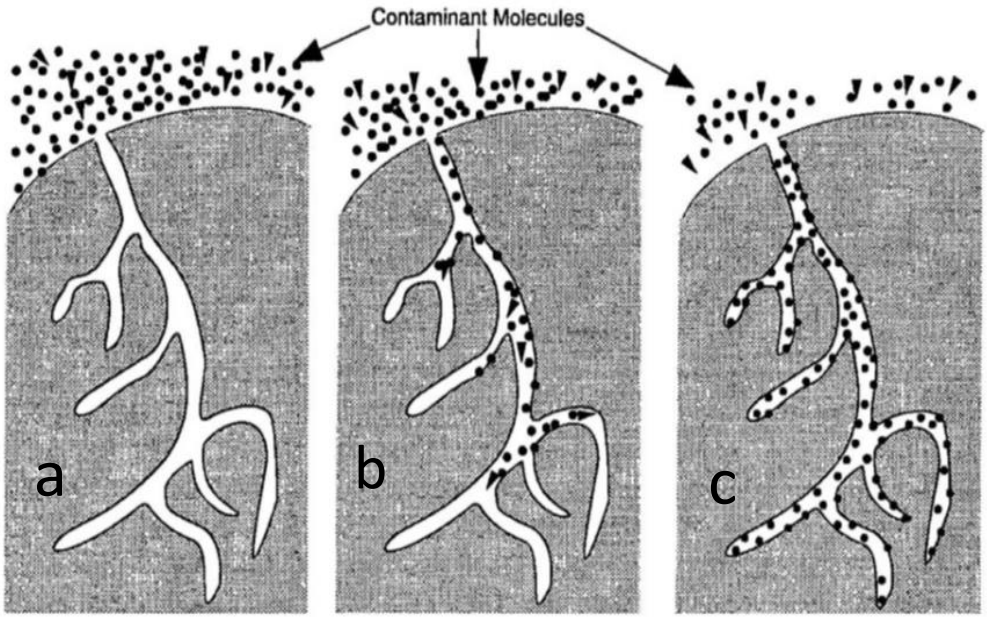

Figure 2.3: Three steps of adsorption mechanism: a) diffusion of adsorbate to adsor-bent surface b) migration into pores of adsorbent c) monolayer build-up of adsorbate on adsorbent. (Repo, 2011)

2.4.7.2. Physisorption and chemisorption

The nature of adsorption depends upon the forces, which act between adsorbent and adsorbates. The adsorption forces are a key factor in defining whether the adsorption is physical or chemical. Occasionally, it is complicated to identify what type of adsorption is predominating in a certain situation. Sometimes it might be a combination of chemi-sorption and physisorption. (Fomkin, 2009)

Physisorption

Physical adsorption is reversible and rapid. Molecules are holding to the surface by van der Waals forces of attraction (intermolecular forces and inter atomic interactions with the energy of 10-20 kJ/mol). Therefore, the lack of interaction energy may break the bond between adsorbent and adsorbate, for example by mechanical movement of the interface. Consequently, the most valuable parameters for physicsorption are the pore size, pore structure, pore volume, and surface area. Physisorption prevails at low tem-peratures, and activation energy is 5-10 Kcal/mol.

Chemisorption

A specific surface area of phases, types of active sites, number of active sites, and stability of active sites are predominantly valuable for chemisorption. Chemical adsorption occurs because of chemical reaction between molecules and atoms of the adsorbate and adsorbent. Chemisorption is irreversible because chemically adsorbed molecules are not able to move on the surface of within interface. The main advantages are high selectivity of separation and the ability to treat exceptionally small concentrations of solute. Chemisorption accelerates by elevated temperature where activation energy varies between 10-100 Kcal/mol. (Sharma, 2013).

2.5. Factors affecting adsorption process

2.5.1. pH

The pH value of the metal solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. The pH of the solution would affect both aqueous chemistry and surface binding sites of the adsorbents. The effect of pH in turn depends on the charge on the adsorbent surface. If the adsorbent surface is negatively charged, at lower pH, the large number of H^+ ions present neutralizes the negatively charged adsorbent surface, thereby reducing hindrance to the diffusion, and a

better adsorption is obtained. If the surface charge of the adsorbent is positively charged, the H^+ ions may compete effectively with the cations of the solution causing a decrease in the amount of metal ion adsorbed (Jiaping, 2012).

2.5.2. Contact Time

The amount adsorbed on to the adsorbent is in a state of dynamic equilibrium with the amount desorbed from the adsorbent. The time required to attain this state of equilibrium is termed as the equilibrium time. The amount adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under the operating conditions (Jiaping, 2012).

2.5.3. Adsorbent Dosage

The concentration of both the metal ion and the sorbent is a significant factor to be considered for effective adsorption process. The adsorbent dosage is an important parameter because this determines the capacity of an adsorbent. It determines the sorbent and sorbate equilibrium of the system. The effect of adsorbent dosage on adsorption was studied by varying the amount of adsorbents and keeping the other parameters constant. According to (Joshi, 2009) investigation, chromium uptake rose with an increase in sorbent. This appears to be due to increase in the available binding sites, which is the surface area of adsorbent in the biomass for the compellation of chromium. However, the chromium uptake decreased gradually when the sorbent concentration exceeding more. Accordingly, the chromium (III) ion in solution has been decreased drastically with the increase in the sorbent dosage.

2.5.4. Concentration

Different initial metal concentrations and a fixed concentration of biomass were used to calculate adsorption capacity. The initial and final concentrations of the solutions were measured by Atomic absorption spectrophotometer. These data were used to calculate the adsorption capacity of the adsorbent (Azouaou et al., 2010; Mausumi et al., 2006; Mohammad Mehdi et al., 2011).

2.5.5. Effects of temperature adsorption

An increasing adsorption temperature leads increasing of particle movements at the surface of the adsorbent and this phenomenon facilitates the detachment of Cr (VI) from adsorbents (Adhena et al, 2014.

2.5.6. Effect of Porosity Adsorbent

The adsorption performance is dependent on the condition of internal surface accessibility. A very important and decisive property of adsorbent materials is the pore structure. The total number of pores and their shape and size determine the adsorption capacity and even the rate of adsorption. According to the IUPAC recommendation, microspores are pores of a width not exceeding 2 nm, mesopores are pores of a width between 2 and 50 nm, and Macropores are pores of a width greater than 50 nm. A further classification involves ultra-micropores, which are pores of a width less than 0.7 nm. The specific surface area of Macropores adsorbents is very small. Therefore, adsorption on this surface is usually neglected. In the case of mesopores, the adsorbent surface area has a distinct physical meaning. Mono- and multilayer adsorption takes place successively on the surface of mesopores, and adsorption proceeds according to the mechanism of capillary adsorbate condensation. Specific surface area, pore volume, and pore size distribution are basic parameters characterizing mesopores. Mesopores and Macropores play an essential role in the transport of adsorbate molecules through the micropores. The sizes of micropores are usually comparable to those of adsorbate molecules. Consequently, adsorption in micropores is essentially a pore-filling process. Therefore, the volume is the main controlling parameter for adsorption in micropores. Considering also that most of the total surface area is found in the micropores and the contribution of Macropores to the total surface area is very low, the contribution of micropores to adsorption would be expected to be higher (Cecen, 2012).

2.6. Adsorption process modeling

Adsorption modeling helps to identify the removal efficiency of adsorbent. Adsorption modeling is applied to describe the experimental data by using adsorption isotherm and kinetic models. (Repo E. 2011.)

2.6.1. Adsorption Isotherms

Equilibrium isotherm model equations such as Langmuir and Freundlich are used to describe experimental adsorption data in the batch model to describe the relation between adsorbate on the surface of adsorbent that is the amount of species adsorbed per unit mass of adsorbent and concentration solute left in the solution **(**Gautam et al., 2014**).** Each adsorption equilibrium state is uniquely defined by the variables adsorbate concentration, adsorbed amount also referred to as adsorbent loading and temperature. For a single-solute system, the equilibrium relationship can be described in its general form as equation 2.1.

$$qeq = f(Ceq, T) \_\_\_\_\_ 2.1$$

Where Ceq is the adsorbate concentration in the state of equilibrium, q_{eq} is the adsorbed amount (adsorbent loading) in the state of equilibrium, and T is the temperature.

2.6.1.1. Langmuir Adsorption Isotherm

Langmuir adsorption isotherms are widely used to describe the relationship between the amount of adsorbate adsorbed onto the adsorbent, its equilibrium concentration in aqueous solution and based on three assumptions: (i) the surface of the adsorbent is in contact with a solution containing an adsorbatewhich is strongly attracted to the surface; (ii) the surface has a specific number of sites where the solute molecules can be adsorbed; (iii) the adsorption involves the attachment of only one layer of molecules to the surface, i.e. monolayer adsorption (Gautam et al.,2014).The Langmuir equation is:

$$qe = \frac{qmaxKLCe}{1 + KLCe} \_\_\_\_\_ 2.2$$

Whereqe is the amount of metal ions adsorbed per gram of adsorbent at equilibrium (mg g^{-1} dry weight), qmax is the maximum amount of the metal ion per unit weight of the adsorbent to form a complete monolayer on the surface-bound at high C_e, C_e is concentration of metal ions in solution at equilibrium and KL is a Langmuir constant.The linear form is

$$\frac{Ce}{qe} = \frac{Ce}{qmax}\frac{1}{KLqmax} \_\_\_\_\_ 2.3$$

The value of qmax and KL computed from slope and intercept of the Langmuir plot of Ce/qe versus C_e. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter RL, which is a dimensionless constant [separation factor] (Dada, 2012).

$$RL = \frac{1}{KLCo} \_\_\_\_\_ 2.4$$

Where C_o initial concentration R_L value indicates the adsorption nature to be either unfavorable if RL>1, linear if RL=1, favorable if $0<R_L<1$ and irreversible if $R_L = 0$.

2.6.1.2. Freundlich Adsorption Isotherm

At lower concentrations, an alternate isotherm developed by Herbert F. Freundlich frequently describes the data better. Freundlich isotherm describes that the ration of the amount of solute adsorbed onto a given mass of adsorbent to the concentration of solute in the solution is not constant at different

concentrations. The empirical Freundlich model also considers monomolecular layer coverage of solute by the adsorbent. However, it assumes the adsorbent has a heterogeneous surface so that binding sites are not identical. This model takes the following form for a single component adsorption

$$qe = KfCe^{\frac{1}{n}} \_\_\_\_\_ 2.5$$

Where C_e = the equilibrium concentration of adsorbate (mg/L), q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g), Kf and 1/n are Freundlich constants. K_f and n are indicators of adsorption capacity and adsorption intensity respectively. The linear form is:

$$logqe = logKf + \frac{1}{n} logCe \_\_\_\_\_ 2.6$$

If n =1 then the partition between the two phases are independent of the concentration. If the value of 1/n is below one, it indicates a normal adsorption. On the other hand, 1/n being above one indicates cooperative adsorption.

2.6.2. Adsorption Kinetics Models

The prediction of adsorption rate gives important information for designing batch adsorption systems. Predicting the rate at which biosorption occurs for a given system is another important factor in biosorption system design, since adsorbate residence time and the reactor dimensions should be in accordance with the systems kinetics. In spite of the importance of biosorption equilibrium studies, that determine the efficiency of the process, kinetic models were used to elucidate the mechanism of biosorption together with its rate controlling steps.

Furthermore, data on the kinetics of heavy metal uptake are necessary to select the best conditions for full-scale biosorption process. The kinetics of adsorption was studied by using first order, and second order models. These models take into account the adsorbed quantities that will enable us in determining the reactor volume.

2.6.2.1. Pseudo-first-order Kinetic Model

The pseudo first order rate equation is:

$$\frac{dq}{dt} = K1(qe - qt) \_\_\_\_\_ 2.7$$

Where k_1 is the rate constant for the pseudo-first-order kinetic equation and q_e and q_t are amounts of solute adsorbed per unit adsorbent at equilibrium and at time t, respectively (Agnieszka and Dorota, 2016).

The linear form of equation 2.8 expressed in the form of:

$$\log(qe - qt) = logqe - \frac{K1}{2.303}t \_\_\_\_\_ 2.8$$

2.6.2.2. Pseudo-second-order Kinetic Model

The pseudo-second-order rate equation is:

$$\frac{dqt}{dt} = K2(qe - qt)^2 \_\_\_\_\_ 2.9$$

Where k_2 is the rate constant for the pseudo-second-order kinetic equation and qe and qt are the amounts of solute adsorbed per unit adsorbent at equilibrium and at time t, respectively (Albadarin, Chirangano et al., 2012). The linear form expressed as in the form of:

$$\frac{t}{qt} = \frac{1}{K2qe2} + \frac{t}{qe} \_\_\_\_\_ 2.10$$

3. MATERIALS AND METHODS

3.1. Characterization of *Moringa olifera* seedpod

3.1.1. Materials

All the equipment is used during the experimentation were Plastic bag, Beaker, Digital balance; magnetic stirrer and crucible were used during batch tests. Modified sample was dried in hot air oven at 105^{o}c for 12hr; electrical furnace was used to determined ash and volatile content of the samples. Fourier transform infrared (FTIR) spectra were recorded using (Perkin Elmer, Spectrum 65FT-IR spectrophotometer) to analyze the functional groups present in the samples and (X-ray Diffraction XRD) used to identify the crystalline or amorphous properties of the *Moringa olifera* seedpod.

In this study, all the chemicals were used analytical reagent graded. Nitric acid (HNO_3) and methanol were purchased from chemical PLC and nitric acid HNO_3 and methanol solution, which were used for modifying the *Moringa oleifera* seedpod.

3.1.2. Methods

3.1.2.1. Raw material preparation

After sourcing, the seeds were removed from the fruit (called drumsticks) and pods were sun dried for about 1week. When satisfactorily dried, the pods were grinded in to powder using a mechanical grinder. The final grinded sample was then sieved through octagon sieve to obtained appropriate particle size and the fraction between125 to 250µm was separated for use in modification process. Then the powdered *Moringa oleifera* seedpod was modified or treated with 0.1M HNO_3 with continuous stirring for 2hr to remove metals from the bi-adsorbent and increase its surface area. After the acid treatment, the adsorbent (about 50g) was extracted with 500mL methanol to remove inorganic and organic matter from the sorbent surface. In addition, the adsorbent was washed with distilled water, dried at 105˚C for 12hr in oven and finally stored in bottle for use.

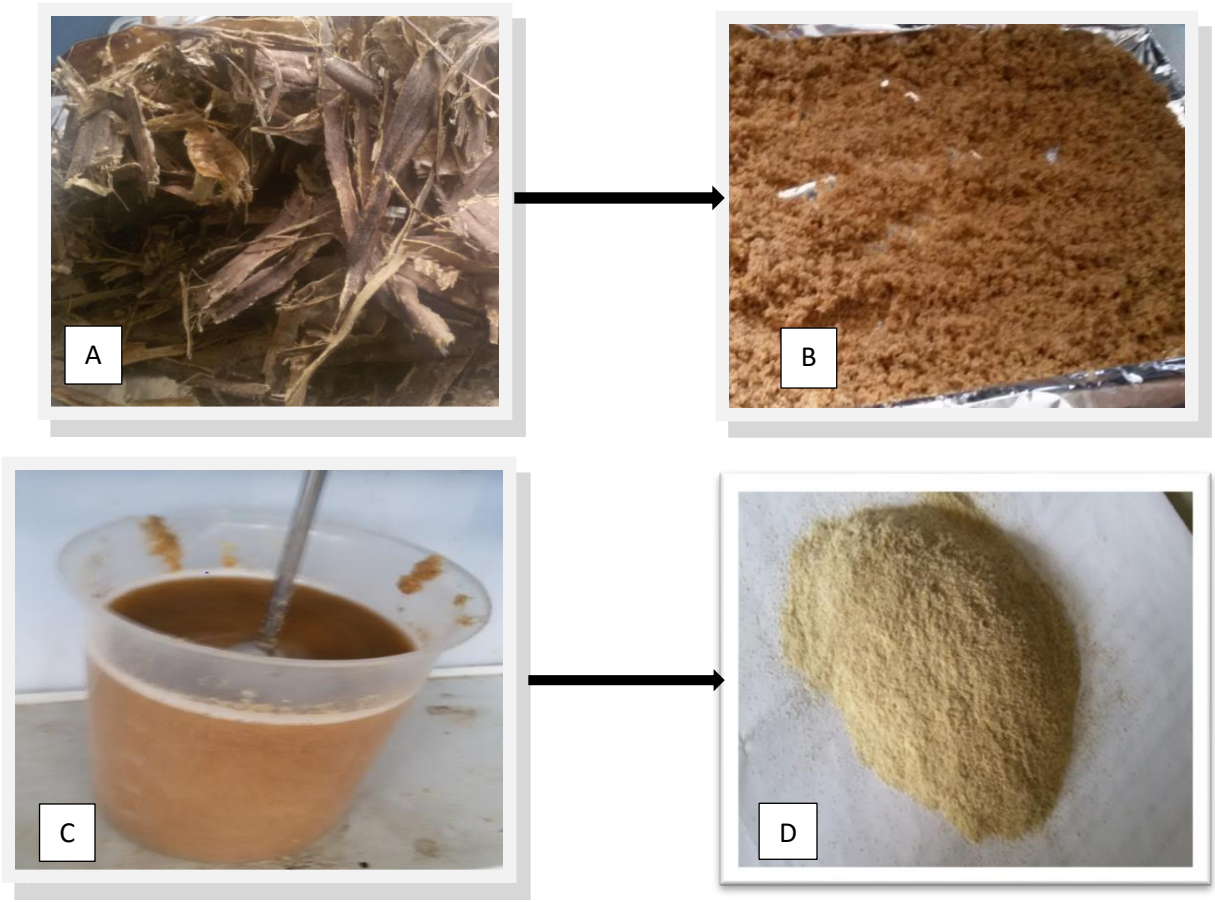

Figure 3.1: Raw material preparation (A) Raw MOSP, (B) Powdered MOSP, (C).Modification process and (D). MOSP after modification.

3.1.2.2. Characterization of Bio-sorbent (Moringa olifera seedpod)

3.1.2.2.1. Moisture content

A crucible was taken and weighed. 2g of sample (MOSP) was added in the crucible and weighed. It was kept in hot air oven at 105°C for 24hr. It was taken out and kept in the desiccators. Then the weight was measured and the moisture content was calculated as:

$$M = 100 \times \frac{(B - F)}{(B - G)} \quad \text{3.1}$$

Where, M = moisture content (%), B= mass of crucible plus sample, F = mass of crucible plus dried sample, G = mass of empty crucible

3.1.2.2.2. Ash content

2g of sample was take in crucible and weighed. The sample was kept in a muffle furnace for 2hr at a temperature of 550°C. Then, it was taken out and kept in desiccators for half an hour to cool down. Then, again, the weight was measured and ash content was calculated as:

$$M = 100 \times \frac{(B-G)}{(B-G)} \quad \text{3.2}$$

Where, A = Ash content, B= Mass of crucible plus sample F= mass of crucible plus ash sample (after heating), G = mass of empty crucible. .

3.1.2.2.3. Volatile Matter

A crucible was taken and weighed. 2g of sample was added in the crucible and weighed. It was kept in the muffle furnace at a temperature of 650°C for 10 minutes. Then it was taken out and kept in the desiccators for half an hour to cool down. The weight of the sample in crucible was measured again. Percent volatile matter was then calculated as,

$$V = 100 \times \frac{100(B-F) - M * (B-G)}{(B-G) * (100-M)} \quad \text{3.3}$$

Where, V= volatile matter (%), B= mass of crucible plus sample, F=mass of crucible plus ash sample, G = mass of empty crucible, M=3%.

3.1.2.2.4. Carbon Content

Carbon content was calculated as following:

$$\%\text{carbon} = 100 - (\%moiturecontent + \%volatile\ content + \%ash\ content) \quad \text{3.4}$$

3.1.2.2.5. Bulk density determination

Bulk density was determined by measuring the volume of water displaced when a specified weight of sample of *Moringa oleifera* seedpod were dropped in to a graduated measuring cylinder by taking a 100 cm^3calibrated measuring cylinders was washed and dried. 50cm^3 of the water was added to the measuring cylinder and was noted.2g of the sample was transferred into the measuring cylinder and the volume of the increased water level was recorded and then calculates the bulk density.

Volume of water displaced (cm^3) = Final volume – Initial volume

$$\text{Bulk density } \left(\frac{g}{cm3}\right) = \frac{\text{Mass of samples (g)}}{\text{Volume of water displaced (cm3)}} - - - 3.5$$

3.1.2.3. Characterization of MOSP using FTIR and XRD analysis

It helps to study the effect of acid attack and the change that have taken place in the structure of *Moringa oleifera* seedpod and determination of surface oxygen-containing functional group. Functional groups in raw, modified MOSP and chromium loaded MOSP were examine by using the Fourier Transform Infrared (FTIR) method of analysis. The FTIR spectrophotometer was analyzed based on changes in dipole moment resulting from bond vibration upon absorption of IR radiation. It was carried out at room temperature using Spectrum 65FT-IR (Perkin Elmer) in the range 4000-400 cm-1 using KBr pellets. The wave numbers associated to signals in the FTIR spectra from chemical functional groups were determined. XRD analysis was carried out to know the produced product was amorphous or crystal. The diffraction patterns were obtained in the 2θ range from 10-70°.

3.2. Investigate the effect selected process variables on the adsorption performance of MMOSP.

3.2.1. Materials

The equipment's used during the batch adsorption studies were Beaker, Filter paper, pH meter , Digital balance, graduated cylinder, pipettes, magnetic stirrer, incubator shaker were used during batch tests. The initial concentration and the final concentration of the metal remaining on the solution were determined using Atomic absorption spectrometry (AAS).

In this study, all the chemicals were used analytical reagent graded. Which were basic chromium sulfate (Cr_2 $(SO_4)_3$) hydrochloric acid (HCl), and sodium hydroxide (NaOH), Basic chromium sulfate used as a preparation of model stock solution, which represents tannery wastewater containing chromium (III) ion, Hydrochloric acid (HCl) and sodium Hydroxide (NaOH),used for pH adjustment.

3.2.2. Methods

3.2.2.1. Preparation of synthetic wastewater

Synthetic solution of chromium (III) was prepared from basic chromium sulfate (Cr_2 $(SO_4)_3$) by dissolving in demonized water as a model pollutant wastewater from tanning industry. For adsorption, experiment about 150mg/L was prepared from stock solution by dilution in order to obtain the standard

solutions. The pH of solution was adjusted either 0.1M HCl or 0.1M NaOH solution using pH meter before adsorption process, to control the pH at the required value.

Figur 3.2. Synthetic solution of Basic Chromium Sulfate (A) model and(B) stoke solution

3.2.2.2. Batch Adsorption Process studies

The experiments were carried out in the batch mode adsorption process to analyze removal capabilities of prepared MOSP at room temperature. Using the 250mL stopper conical flask containing 100mL of model pollutant solution of batch adsorption studies was carried out at the desired pH value, contact time and adsorbent dosage. The pH of solution was monitor by adding 0.1M of HCl and NaOH solution. Amount of prepared sorbent was add to each flask containing model pollutant of wastewater and it was agitate intermittently by mechanical shaking at speed of 200rpm for a contact time of from 45 min to maximum time 135min at room temperature. After adsorption process, separation of the sorbent and solutions was carried out by filtration process using vacuum filtration unit and the filtrate was stored in sample cans to determine the metal ion concentration of chromium, to analysis removal percentage chromium (III) ion. The experiment was carried out for different sorbent of dosage (0.3, 0.65, and 1) g, pH (3, 5.5, and 8) and contact time (45, 90, and 135) min. The detailed description of experimental procedure of batch adsorption studies was shown in the Figure 3.3.

1. Before the MMOSP added into the Cr (III) solution, the initial Cr (III) concentration was measured and the pH of Cr (III) solution was adjusted.

2. Then the required amount of MMOSP was mixed with the Cr (III) solution in the 250mL flask.

3. The Flasks were placed in the incubator shaker at 200rpm and 25^{o}c for mixing the solution properly for required period.

4. Remove the samples of this mixture from the shaker at different time intervals (45, 90,135) min, were collected, filtered, and stored for analysis.

5. Finally the stored samples were analyzed using AAS to identify the final Cr (III) concentration of the sample solution.

Figure 3.3: Experimental procedure of batch adsorption studies.

Figure 3.4: Batch adsorption set up (A) Samples before Adsorption and (B) Samples after adsorption

3.2.2.2.1. Effect of pH

The effect of pH on the adsorption of chromium from model pollutant solutions (100mL) of concentration 150mg/L in conical flasks 250mL were adjusted to desired pH (3, 5.5 and 8) values and mixed with constant amount of adsorbent, which is varied with pH varied and agitated at a preset equilibrium time with constant agitated speed 200rpm of adsorption process.

3.2.2.2.2. Effect of Contact Time

For the determination of the rate of chromium bio-sorption by adsorbent from a model pollutant of 100mL at 150mg/L in a conical 250mL flask, the solution was analyzed for residual chromium at different time intervals (45, 90 and 135) min. The pH and the adsorbent dosage kept at constant, but which varied according to the contact time varied, and the process was taken under constant shaking speed, 200rpm, and 25^{o}c.

3.2.2.2.3. Effect of Adsorbent Dosage

The effect of adsorbent dosage on t e adsorption of chromium was studied at different dosages ranging (0.3, 0.65 and 1) g with chromium concentrations of 150mg/L in pollutant solution. The contact time and the pH were kept constant, which is varied according to the variation of adsorbent dosage added to model wastewater pollutant and adsorption is process was done at constant shaking speed 200rpm and 25^{o}c.

3.2.2.3. Experimental design for adsorption.

Batch experiment study was conducted to show the statistical significance of or influence of the study variables (adsorbent dosage, contact time and pH) on percentage Cr (III) removal from aqueous solution. Response surface study type with initial of General Factorial design was applied to generate full factor combinations effect and easily to obtain the optimum adsorption of metal ions using Design of Expert (DOE) software version 7.0.0.

3.2.2.3.1. Description of experimental for factors and response variables

A standard response surface methodology design called General Full Factorial design (GFFD) was applied to study the variables for adsorption of chromium in a batch process. Numbers of observations

were 27 (a complete 3^3factorial design experiments). The purpose was to determine the effect of all factors on percentage Cr (III) removal.

3.3. Determination of the Percentage Removal and adsorption capacity

3.3.1. Determination of the Percentage Removal of chromium (III) ions using MMOSP.

Adsorption studies were carried out at room temperature and constant agitation speed for a known initial concentration of the chromium (III) solution. The supernatant liquid was filtered and the concentrations of Cr (III) ions left in the pollutant wastewater were determined using atomic adsorption spectrophotometer. The adsorption efficiency values was recorded by atomic adsorption spectrophotometer (AAS) were described the ability of modified *Moringa olifera* seedpod to adsorb chromium (III) ion. It was used to determined metal ion. Therefore, the removal efficiency of the adsorbent was carried out using:

$$removal\ (\%) = \frac{Co - C}{C0} \times 100\% \quad \text{3.6}$$

Where, Co and C = chromium ion content of wastewater (mg/L) before and after adsorption treatment, respectively.

3.3.2. Determination of the Adsorption Capacity of chromium (III) ions using MMOSP.

The equilibrium adsorption capacity of adsorbent (q_e) was found by using the values of adsorption capacity of adsorbent at a particular time (q_t) for initial Cr(III) concentrations. When q_t value became constant after a certain period, a constant value of q_t was termed as equilibrium sorption capacity, which is point maximum MOSP to adsorb chromium ions. The amount of chromium (III) ions adsorbed per gram of bio-sorbent was calculated using the following expressions:

$$qe = \frac{(co - ce)V}{M} \quad \text{3.7}$$

Where, q_e is the amount of Cr (III) sorbed per gram of adsorbent, C_o and C_e are the initial and equilibrium or final concentrations of Cr (III) (mg/L) respectively, V is the volume of solution (L), and m is the mass of adsorbent (g).

3.4. Adsorption isotherms

Adsorption isotherms was defined as a graphical representation showing the relationship between the amount adsorbed by a unit weight of adsorbent and the amount of adsorbate remaining in a test medium at equilibrium, and it shows the distribution of an absorbable solute between the liquid and solid phases at various equilibriums. It is also helpful in model prediction for analysis and design of an adsorption process.

3.4.1. Langmuir Isotherm

The Langmuir adsorption isotherm is perhaps the best known of all isotherms describing adsorption. The Langmuir model was obtained under the ideal assumption of a totally homogenous adsorption surface (Bilgili, 2006) and represented as follows (Langmuir, 1918):

$$qe = \frac{qmKLCe}{1 + \mathrm{KLCe}} \quad \text{3.8}$$

Where C_e is the equilibrium concentration (mg/L), q_e is the amount of metal ion adsorbed (mg/g), q_m is the q_e for a complete monolayer (mg/g), and K_L is the constant related to the affinity of the binding sites and the energy of adsorption (L/mg).

3.4.2. Freundlich Isotherm

The Freundlich isotherm model worked based on the assumption that the adsorption of adsorbate occurs in multilayer on heterogeneous adsorbent surfaces since the active sites of adsorbent have heterogeneous surface energy. The model was expressed linearly in Eq.3.9 as follow that multilayer Cr (III) adsorption occurs on heterogeneous surfaces of adsorbents.

$$\mathrm{qe} = \mathrm{KfCe}^{\frac{1}{n}} \quad \text{3.9}$$

Where, q_e is equilibrium loading in mg/g; C_{eq} equilibrium concentration in mg/L, K_f Freundlich constant in mg/g, and n, Freundlich exponent.

3.5. Adsorption Kinetics Models

The prediction of adsorption rate gives important information for designing batch adsorption systems. Predicting the rate at which biosorption occurs for a given system is another important factor in biosorption system design, since adsorbate residence time and the reactor dimensions should be in

accordance with the systems kinetics. In spite of the importance of biosorption equilibrium studies, that determine the efficiency of the process, kinetic models were used to elucidate the mechanism of biosorption together with its rate controlling steps.

Furthermore, data on the kinetics of heavy metal uptake are necessary to select the best conditions for full-scale biosorption process. The kinetics of adsorption was studied by using first order, and second order models. These models take into account the adsorbed quantities that would enable us in determining the reactor volume.

3.5.1. Pseudo-first-order Kinetic Model

The pseudo first order rate equation is:

$$\frac{dq}{dt} = K1(qe - qt) \_\_\_\_\_ 3.10$$

Where k_1 is the rate constant for the pseudo-first-order kinetic equation and q_e and q_t are amounts of solute adsorbed per unit adsorbent at equilibrium and at time t, respectively (Agnieszka and Dorota, 2016).

The linear form of Eq. 2.7 expressed in the form of:

$$\log(qe - qt) = logqe - \frac{K1}{2.303}t \_\_\_\_\_ 3.11$$

3.5.2. Pseudo-second-order Kinetic Model

The pseudo-second-order rate equation is:

$$\frac{dqt}{dt} = K2(qe - qt)^2 \_\_\_\_\_ 3.12$$

Where k_2 is the rate constant for the pseudo-second-order kinetic equation and q_e and q_t are the amounts of solute adsorbed per unit adsorbent at equilibrium and at time t, respectively (Albadarin, Chirangano et al., 2012).

The linear form expressed as in the form of:

$$\frac{t}{qt} = \frac{1}{K2qe2} + \frac{t}{qe} \_\_\_\_\_ 3.13$$

4. RESULTS AND DISCUSSIONS

4.1. Characterization of *Moringa oleifera* seedpod

A proximate analysis was perform for both the prepared raw and modified *Moringa oleifera* seedpod to analyze its different physical characteristics such as moisture content, volatile matter, ash content and bulk density .

Table 4.1: The proximate analysis result of MOSP and MMOSP.

Parameter Test	Result	
	Raw MOSP	Modified MOSP
Moisture content	5.20%	4.20%
Ash content	35.02%	27.20%
Volatile content	39.97%	32.21%
Fixed carbon	19.83%	36.62%
Bulk density	1.67g/cm^3	1.25g/cm^3

4.1.1. Moisture content of MOSP.

The laboratory results of the moisture content of raw MOSP and MMOSP were determined to be 5.20 and 4.20 % respectively, whereas dry matter content of MMOSP samples greater than that of raw MOSP. The moisture content of a sample refers to the percentage of water content of the sample. These gave a tangible and substantial amount of organic matter needed was removed during modification. The moisture content of both raw and modified MOSP were slightly lower than the value reported in the literature, 6.84 %.(Mahmoud et al., 2012)

4.1.2. Ash content of MOSP.

The proximate analyses of raw MOSP and MMOSP as presented in the Table (4.1) shows a treatment of modification of MOSP resulted in the removal of the inorganic constituents and reduction of oil from raw MOSP therefore the amount of ash content of raw MOSP is higher than that of modified. The lower

the ash content the better the starting material for adsorption. The ash content of both raw and modified are nearly approached to stated values 28.62% (Lahore, 2017).

4.1.3. Volatile content of MOSP.

The percentage of volatile content for MOSP and MMOSP samples was reduced from 39.97 to 27.21 % as shown in Table (4.1). The lower volatile content of the modified MOSP showed that some of organic molecules of the material were attached and it is stable for adsorption experiment of Cr (III) ions from aqueous solution.

4.1.4. Bulk density of the MOSP.

Bulk densities (g/cm^3) for raw MOSP and MMOSP were $1.67 g/cm^3$ and $1.25 g/cm^3$respectively. These values are higher than the minimum requirement ($0.25 g/cm^3$) for application in removal of pollutants from wastewater. It was observed that the modified *Moringa oleifera* seedpod had a lower bulk density than raw *Moringa oleifera* seedpod, which was$1.25 g/cm^3$. Bulk density is an important physical parameter especially when an adsorbent is to be investigated for it filterability. Higher density provides greater volume activity and normally indicates high quality adsorbent (Kundu; Gupta, 2006).

4.1.5. X-ray Diffraction (XRD) Analysis of *Moringa oleifera* seedpod.

X-ray diffraction (XRD) is a material characterization technique that can be useful for analyzing the lattice structure of a material. It investigated amorphous properties of a MOSP. The XRD patterns of the adsorbents were presented in Figure (4.1). Low and high intensity Bragg diffraction peak were observed for the adsorbents. The XRD patterns shows the two major peaks were $2\Theta = 15^0$and $22.5.^0$. The X-ray diffraction (XRD) analysis of MMOSP and Cr(III) loaded MMOSP showed peaks that are highly amorphous in nature.

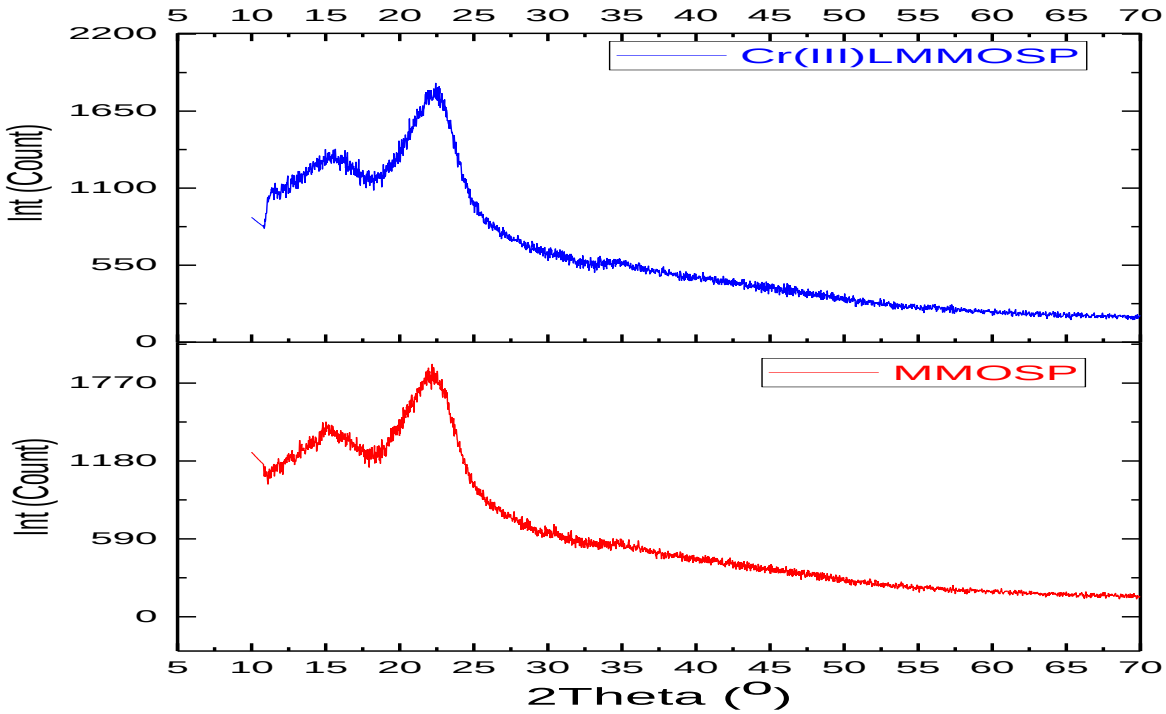

Figure 4.1: XRD pattern of MMOSP and Cr (III) loaded MMOSP

4.1.6. Fourier transform infrared (FT-IR) spectrum analyses of MOSP

Fourier transform infrared (FT-IR) spectroscopic analyses were used to study the main functional groups of raw, modified and Cr (III) loaded Moringaoleifera seedpod. The adsorbents spectra were measured on spectrum 65FT-IR (Perkin Elmer) in the range of 400- 4000 cm-1 using KBr pellets. FT-IR spectra of the adsorbents (raw, modified and chromium (III) loaded *Moringa olifera* seedpod) were shown in Figure (4.2) A B C respectively. The adsorbent materials showed the following bands for raw MOSP or before modification, their spectra of MOSP as shown in Figure (4.2) A the stretching bands around 3436cm^{-1} attributed to the surface of hydroxyl group. The bands at 2929cm^{-1} is due to C-H group of alkenes, at 1639cm^{-1} indicate the presence of C=C from alkenes and N-H from amine groups and C-O from carboxylic acid at 1051cm-1. Changes in intensity and shift in the position of the peaks could be observed in FT-IR spectrum after Cr (III) adsorption on *Moringa olifera* seedpod (figure 4.2 C). The shifting of the peak at 1630 to 1617 cm-1 indicates that the involvement of C=O/C=C in the adsorption process. The peak of raw MOSP at 1051cm-1 (figure 4.2.A) shifted to 1039cm-1(figure 4.2.C). This suggested the involvement of C-O group in the binding of Cr (III).The decrease in intensity and shift of the above-mentioned peaks as shown in Figure (4.2) C could be due to interaction of the Cr (III) with the specific functional groups of *Moringa oleifera* seedpod.

The metal adsorption capacity is influenced strongly by the surface structures of carbon-oxygen and surface behavior of carbon. Similar studies was done with other previously published FTIR dates have shown similar functional groups responsible for metal removal. (Helen and Miranda, 2010).The functional groups responsible for metal removal in *moringa oleifera* seedpod are therefore hydroxyl (OH), C-H of the alkenes, C=C alkenes, and C-O from the carboxylic acids.

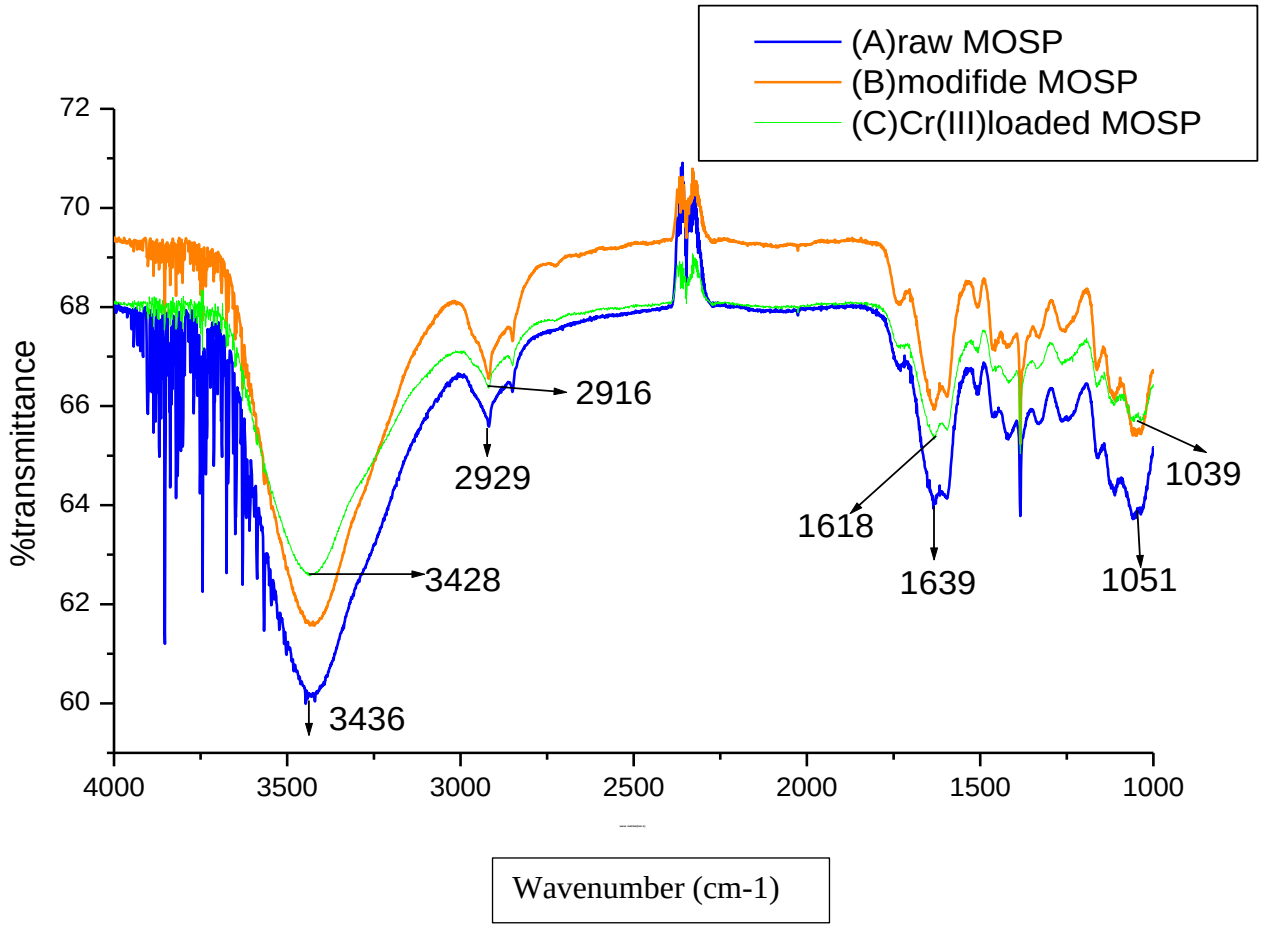

Figure 4.2: FTIR pattern of (A) raw (B) modified and (C) Cr (III) loaded MOSP.

4.2. Analysis of variance (ANOVA) for the design model

The standard analysis of a total number of 27experiments results using quadratic regression analyses. The effects of three independent variables that were adsorbent dosage, pH and contact time with three levels were chosen as independent variables with designated factors as A, B, and C, respectively, and the

variables are presented in Table (4.2). The laboratory experiments were done at a constant initial concentration of pollutant of 150mg/L, shaking speed 200rpm, and room temperature. Design summary three levels and three factors. The design model of the experiments is a quadratic polynomial with no block.

Table 4.2: The designed variables for the adsorption process.

Independent variables	Range and level variables		
	Low	Medium	High
A-MOSP-dosage	0.3	0.65	1
B-PH	3	5.5	8
C-Contact time	45	90	135

The experimental result analysis was done by using analysis of variance of the quadratic regression model for analysis significant model terms. To determine whether the quadratic model is significant, it was required to perform analysis of variance (ANOVA). The probability (P-values) values were used as a device to check the significance of each coefficient, which also showed the interaction strength of each parameter. The smaller the P-values (<0.0001) indicating that the model by design expert highly significance of the corresponding coefficient. F- Value is a test for comparing model variance with residual (error) variance. Model Mean Square divided by Residual Mean Square calculates it. If the variances are close to the same, the ratio will be close to one and it is less likely that any of the factors have a significant effect on the response. The range and level of parameters variables described in Table (4.3).

From the Table (4.3), ANOVA analysis was observed that the Model F-value of 17.42 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, AB, AC, BC, A^2, B^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.The R^2 value provides a measure of how much variability in the observed response values can be explained by the experimental variable and their interaction.

Table 4.3: Analysis of variance (ANOVA) for percentage removal of Cr (III) ions

Source	Sumof Square	Df	Mean Square	F Value	p-value prob>F
Model	593.64	9	65.96	17.42	<0.0001 significant
A-MOSP-dosage	36.04	1	36.04	9.54	0.0067
B-PH	210.95	1	210.95	55.86	<0.0001
C-Contact.time	15.35	1	15.35	4.06	0.0599
AB	23.07	1	23.07	6.11	0.0243
BC	55.56	1	55.56	14.71	0.0013
AC	23.32	1	23.32	6.18	0.0236
A^2	88.18	1	88.19	23.36	0.0002
B^2	132.10	1	132.10	34.98	<0.0001
C^2	9.06	1	9.06	2.40	0.1398
Residual	64.19	17	3.78		
cor total	657.83	26			

Table 4.4: Model adequacy measures

Std.Dev	1.94	R-Squared	0.9024
Mean	93.64	AdjR-Squared	0.8508
C.V%	2.08	Pred R-Squared	0.7252
PRESS	180.76	Adeq Precision	17.292

From the above Table (4.4), The "Pred R-Squared" of 0.7252 is in reasonable agreement with the "Adj R-Squared" of 0.8508."Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable.Your ratio of 17.292 indicates an adequate signal. This model can be used to navigate the design space.

Table 4.5: Regression coefficient and the corresponding 95% CI High and Low

Factors	Coefficient Estimate	Df	Standard Error	95%Cl Low	95%Cl High	VIF
Intercept	100.14	1	.99	98.05	102.23	1.00
A-MOSP-dosage	1.41	1	0.46	0.45	2.38	1.00
B-PH	3.42	1	0.46	2.46	4.39	1.00
C-contact time	0.92	1	0.46	-0.043	1.89	1.00
AB	-1.39	1	0.56	-2.57	-0.20	1.00
AC	-2.15	1	0.56	-3.34	-0.97	1.00
BC	-1.39	1	0.56	-2.58	-0.21	1.00
A^2	-3.83	1	0.79	-5.51	-2.16	1.00
B^2	-4.69	1	0.79	-6.37	-3.02	1.00
C^2	-1.23	1	0.79	-2.90	0.44	1.00

Final Equation in Terms of Coded Factors:

removal efficiency(%) =+100.14+1.41* A+3.42 * B+0.92 * C-1.39 * A * B-2.15* A * C-1.39 * B * C-3.83* A^2-4.69 * B^2-1.23 * C^2 _____4.1

where, A-MOSP-dosage, B-PH , C-contact time

4.2.1. Regression model analysis

The quadratic effect of the model designed from input variable, the comparison of GFFD model of actual and predicted plots for percentage removal of Cr (III) ions using MMOSP was estimated as shown in Figure (4.3). The relationship between actual values and predicted values indicate that the actual values are distributed relatively near to the straight line, this was an indication of better fitting of the model with the experimental data

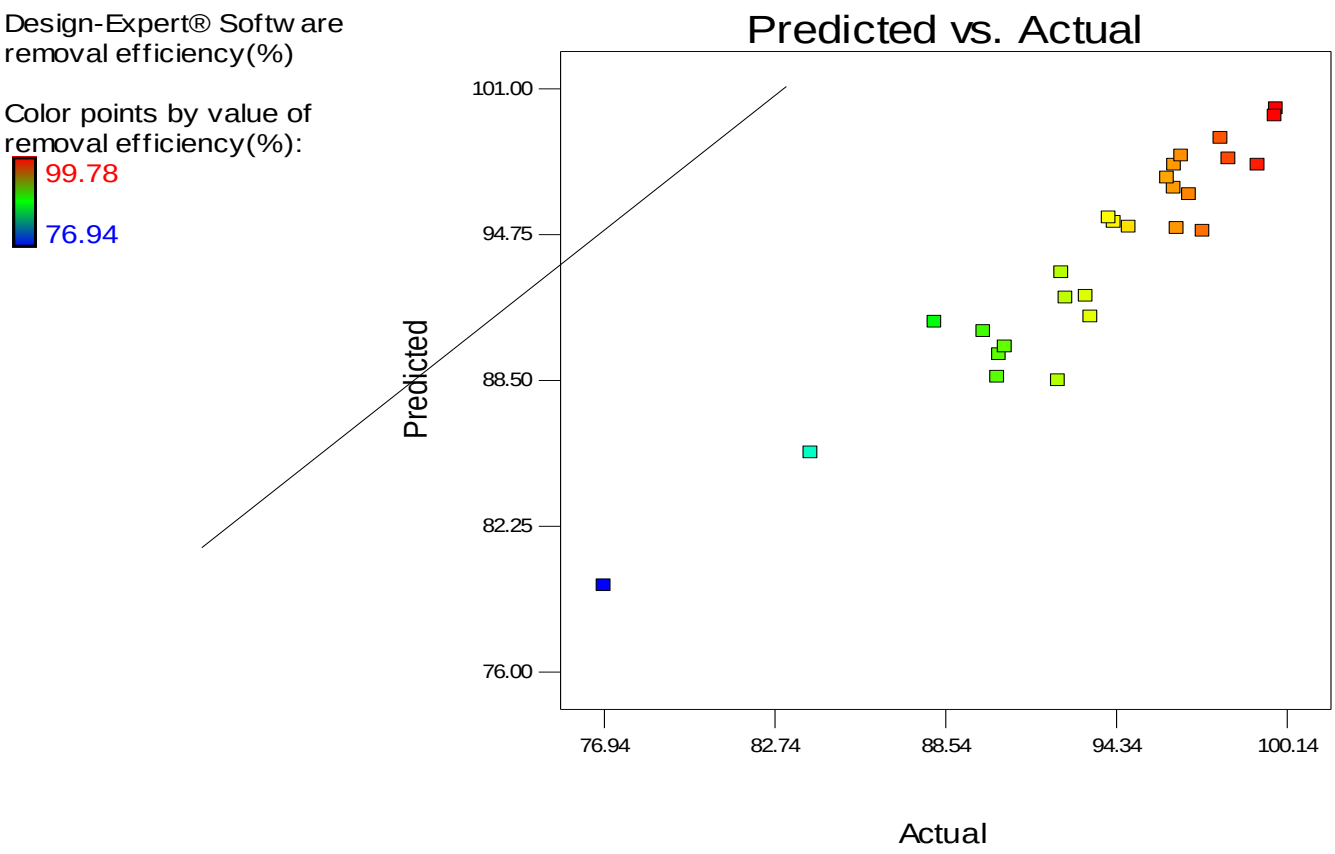

Figure 4.3. The predicted vs. actual and plot for percentage removal of Cr (III) ions using MMOSP

4.3. The Effect of individual Process Variables on Chromium (III) Removal

4.3.1. Effect of MOSP Dosage on Chromium (III) removal.

The relation between the percentage removals of chromium (III) with MMOSP dosage is shown in Figure 4.4. From this curve, it is clear that the percentage removal of chromium slightly increased with the increase of adsorbent dosage. The initial chromium concentrations were set at 150 ppm. The Moringaoleifera seedpod adsorbent was varies from 0.3 g to 1 g. For adsorbent dosage of 0.65g achieved percentage reduction of chromium (III), using MMOSP was more than 99%. Beyond 0.65g, the removal percentage of chromium was almost slowly decreased this is less removal of chromium due to particulate interaction such as agglomeration. Such aggregation leads to a decrease in total surface of the adsorbent, which describes not exposing the surface area to adhere the chromium (III) from the solution rather occupied by agglomerated matter. This result can be explained; when the adsorption dose reached, a certain rate the adsorption site were used up, hence with reduced tendency of the particles to

adsorb any more ions to its surface. Therefore, removal rate of chromium (III) no longer increased. Similar results were found by other researchers. (Reza and Seyedeh, 2011).

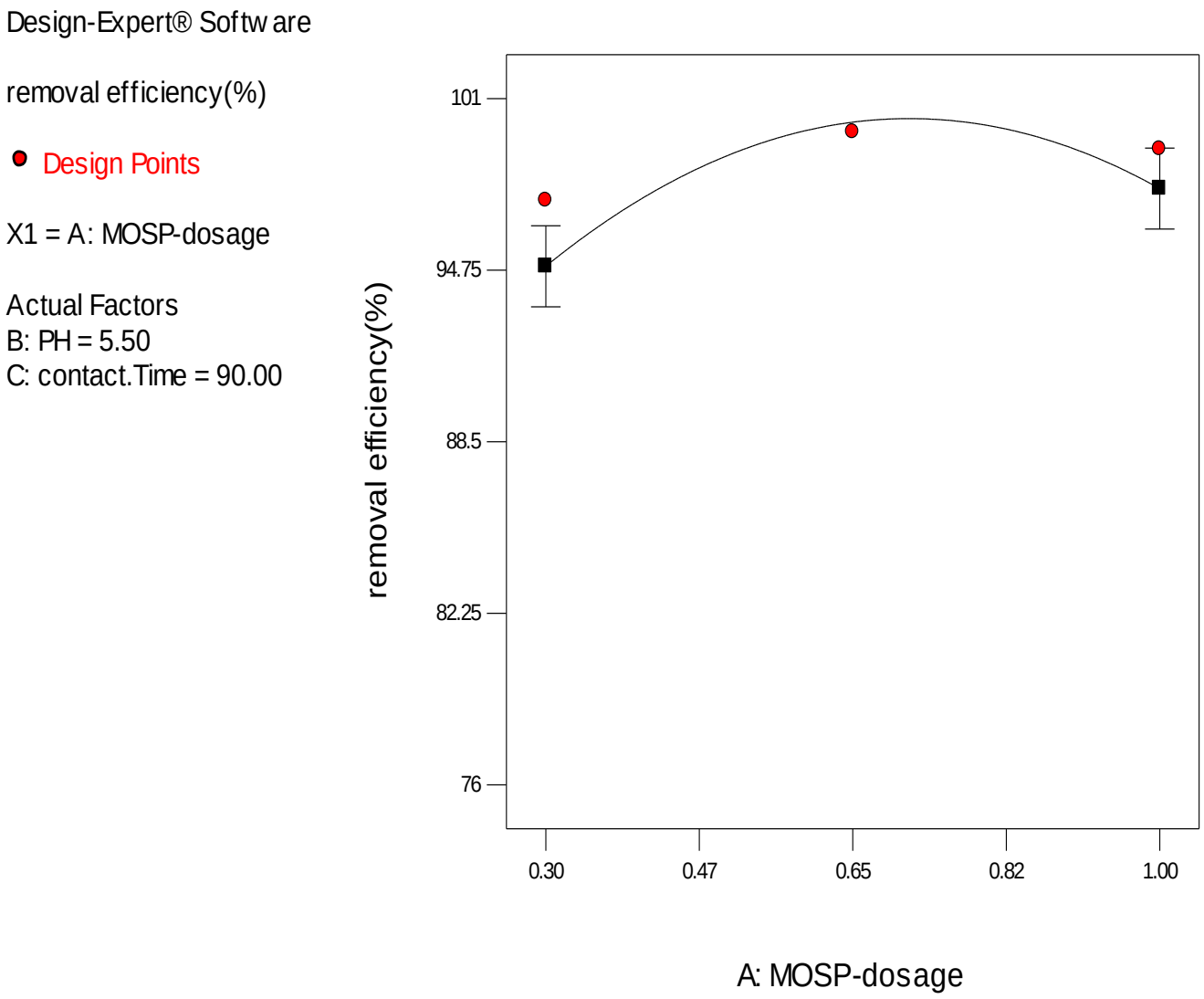

Figure 4.4: Effect of MMOSP-dosage on chromium (III) removal

4.3.2. Effect of pH on Chromium (III) Uptake

The effect of pH on the removal of chromium(III) was shown in the Figure 4.5. It is evident that for Moringaoleifera seedpod the percentage removal of chromium is almost 99.78% at pH 5.5. The percentage removal of chromium ions increased at acidic pH values are present $H^+$and Cr^{3+}ions compete for the active sites of adsorption .From pH 5.5 to 6.75 rates of adsorption chromium made constant value beyond this the efficiency of biosorbent is slightly decreased, because, at high pH chromium (III) ion

was not adhering into the binding's sites of adsorbents. This slight decrease in adsorption at high pH is due to the formation of soluble hydroxyl complexes. These species are adsorbed at the surface of sorbent by ion exchange mechanism with the functional groups present in sorbent or by hydrogen bonding (Rafatullah, 2009). Therefore, the results describe that pH of the solution affects the adsorption efficiency of adsorbent.

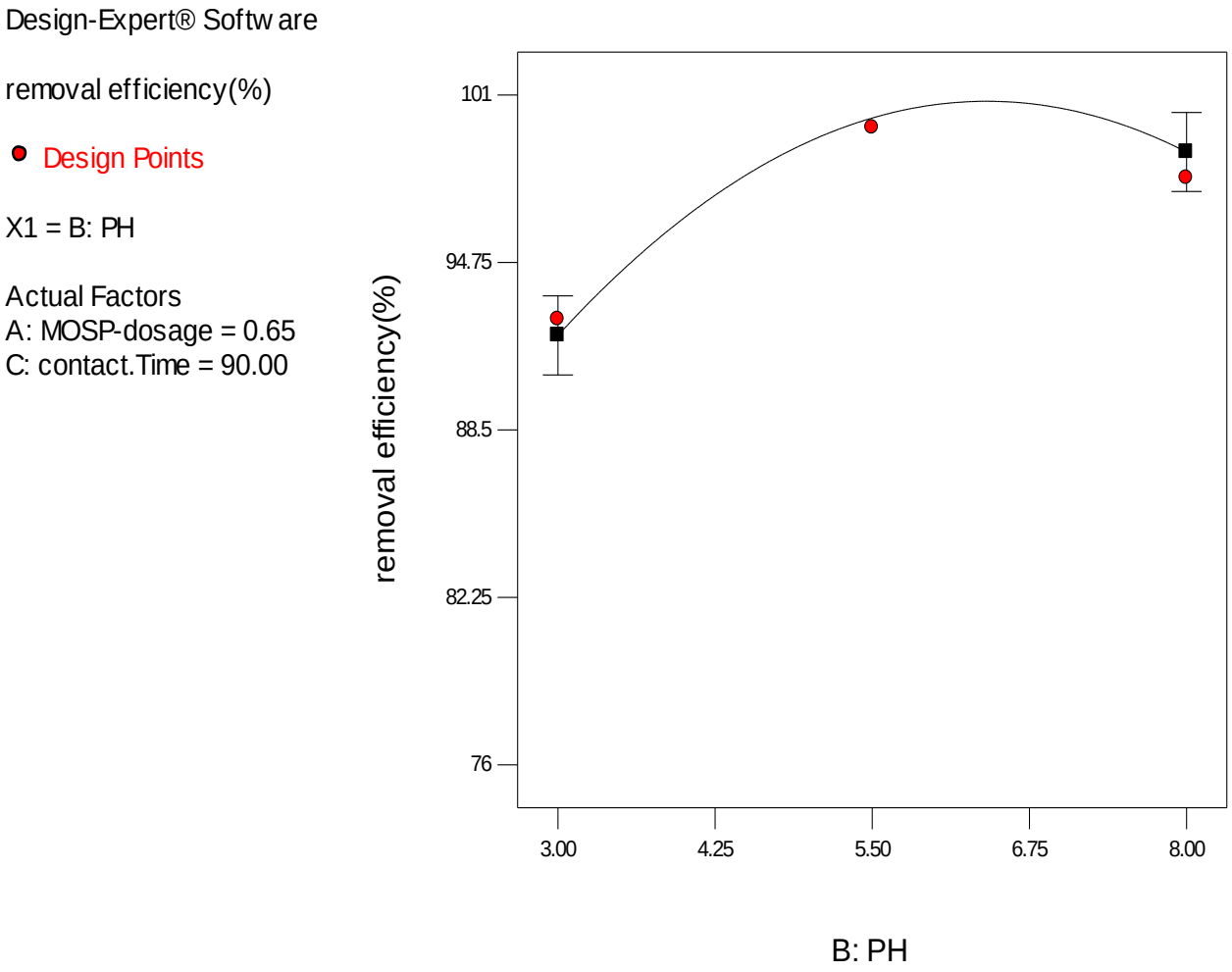

Figure 4.5: Effect of PH on chromium (III) removal using MMOSP

4.3.2. Effect of Contact Time on Chromium (III) removal

The optimum contact time was determined based on the percentage efficiencies. The removal of Cr (III) from solution as a function of time was presented in Figure (4.6). Adsorption capacity slightly increased form 45min to 90min this indicates that chromium (III) ion adsorption efficiency increased with

increasing contact time, beyond that slowly decreasing with time and attains equilibrium at 115min. Probably due to the availability of larger surface area of the MMOSP for the adsorption of these ions and prolonged contact between the sorbent surface and the solute chromium (III) solution. After the active sites of the adsorbent get exhausted when equilibrium is attained, the rate of uptake is controlled by the rate at which the adsorb ate is transported from the exterior to the interior sites of the sorbent particles. Lower adsorption efficiency rate in the latter stage of 115min was due to the difficulty encountered by Cr^{3+} ions in occupying the remaining vacant surface sites because of forces between the solute molecules of the solid and bulk solution. This is same idea with the conclusion of (M. Rafatullah, 2014) in adsorption characteristic of heavy metal ions onto a low cost bio sorbent from aqueous solutions.

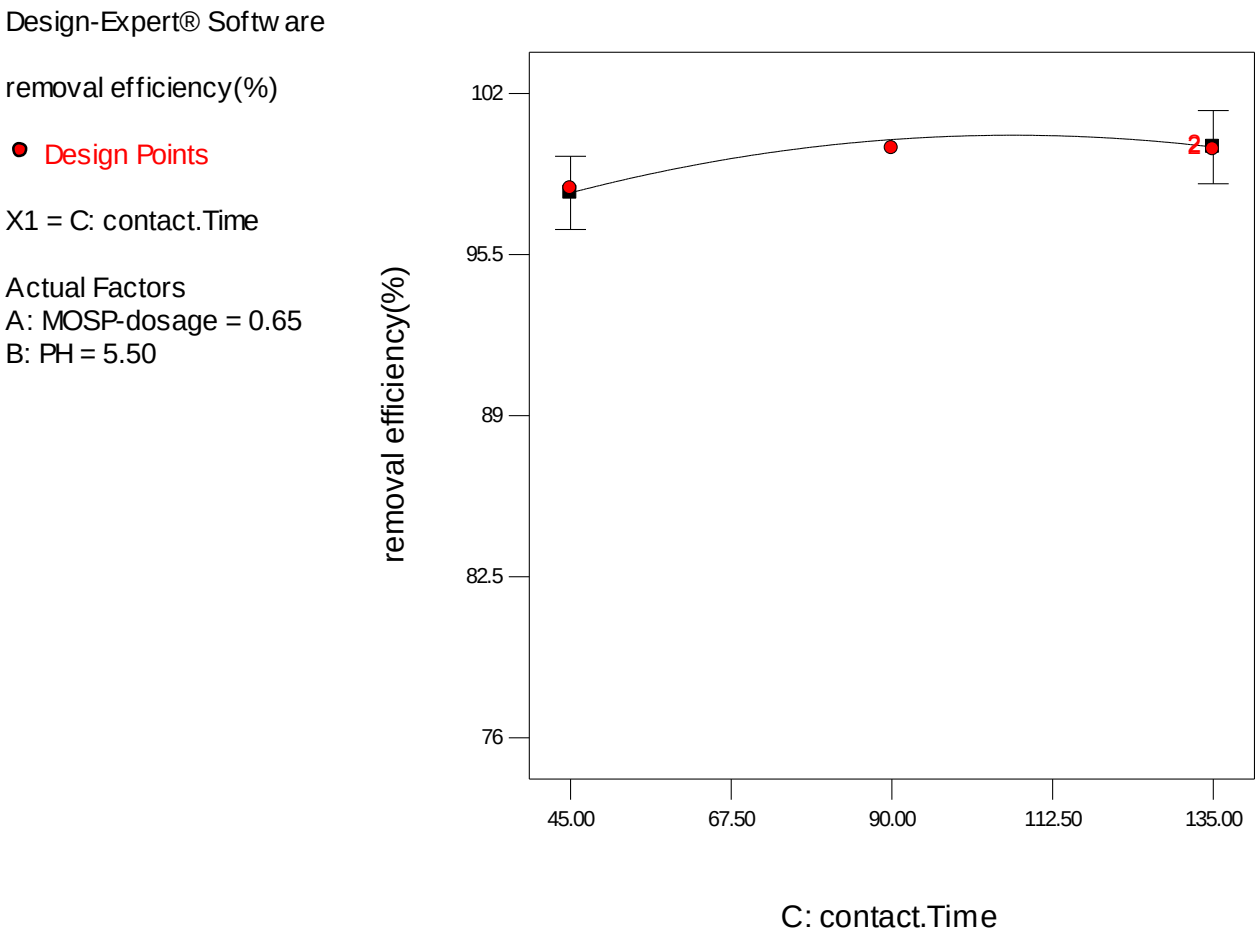

Figure 4.6: Effect of contact time on chromium (III) removal

4.4. Interaction Effects of Process Variables on Chromium (III) removal

The interaction effect of process variables on chromium (III) ion removal using design expert was analyzed using 3D plots of three-dimensional views of response surface as a function of two independent variables and other variables at the center point. These plots can be used in understanding both the main and interaction effects of the independent variables on the response variable.

4.4.1. The Interaction Effect of Adsorbent Dosage and pH

3D plot graph showing predicted the response of chromium (III) ion removal efficiency as a function of adsorbent dosage and pH were shown in figure (4.7). The graph describes that as pH of the solution increases with adsorbent dosage increasing, the percentage of chromium removal efficiency increases 83.97% chromium (III) removal was obtained at sorbent dosage 0.3mg and pH 3 at fixed contact time 90 min. However, removal efficiency increased up to 99.78 % at sorbent dosage increased to 0.65 mg and pH increased to 5.5 at contact time at the center time. In addition, the increase in percentage removal may be due to the complete utilization of all active sites in the adsorbent dosages by lower pH of the solution. Generally, as pH increases at the lower level of adsorbent dosage and as adsorbent increases at the low level of pH gives a positive effect on the chromium removal efficiency.

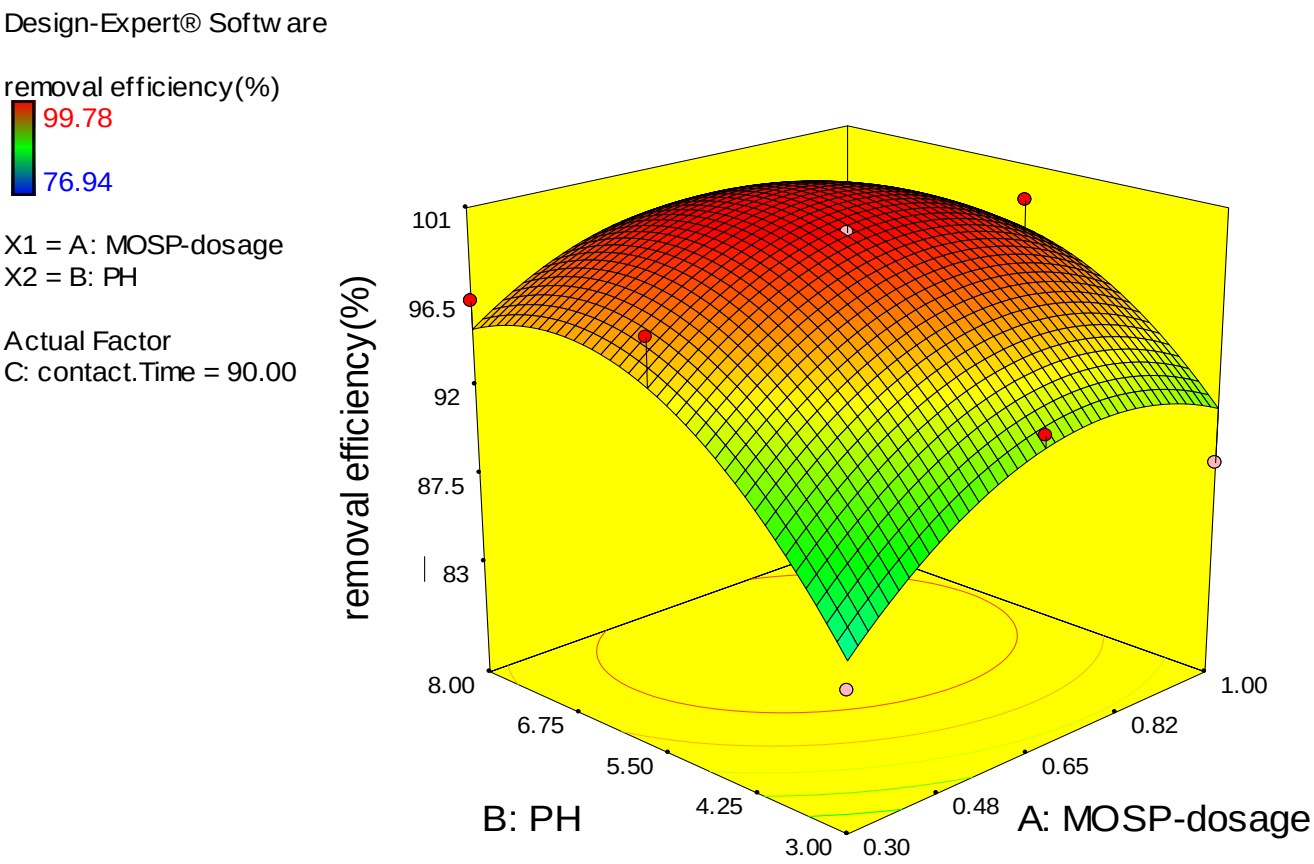

Figure 4.7: 3D plot of the effect of MMOSP dosage and pH on Cr (III) removal efficiency

4.4.2. The Interaction Effect of Adsorbent Dosage and Contact Time

3D shows the effects of the independent variables and their mutual interaction on the removal efficiency of chromium (III) using MMOSP. From the surface response and contour plot, at a definite adsorbent dose of (0.3-0.65)gram, the efficiency of chromium removal efficiency increased slightly and nearly reach a peak, beyond that removal efficiency decreases. However, upon increasing the dose, beyond 0.65g, there is a gradual decrease in the removal efficiency, this because of sorbent a particulate agglomeration this decline active site for adsorption surface area. General, the maximum percentage removal of chromium (III) ion using MMOSP was obtained at a medium value of dosage and higher contact time (90—112.5min). The graph shows that the maximum adsorption (99.78) occurs under dosage value in between 0.65 to 0.82 g, from the figures, as contact time increase at lower adsorbent

dosage gives positive effects on the efficiency of chromium removal and decreases in efficiency at a higher dose with lower contact time.

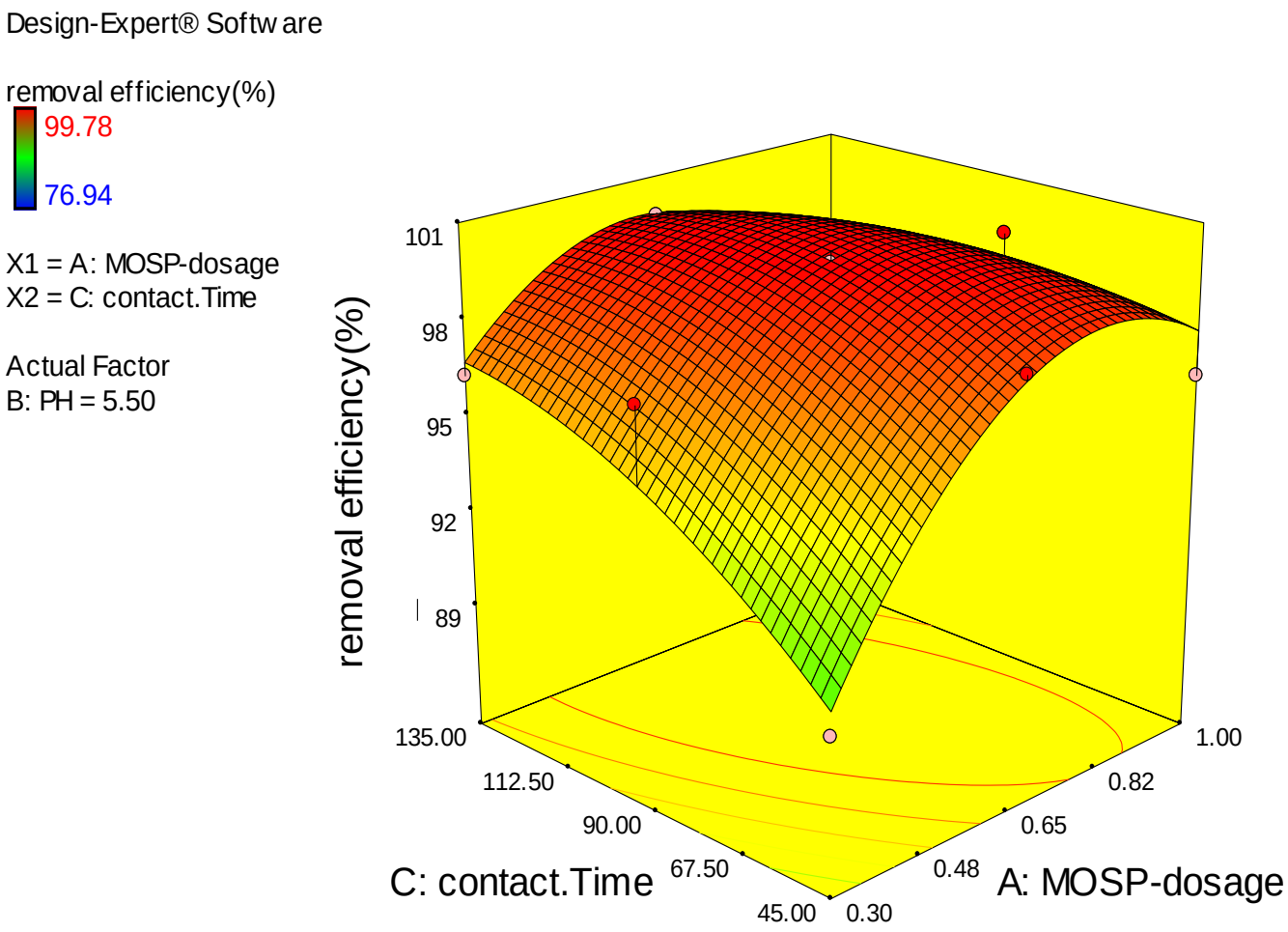

Figure 4.8: 3D plot of the effect of MOSP dosage and contact time on Cr (III) removal efficiency

4.4.3. The Interaction Effect of pH and Contact Time

Figure (4.8) was 3D surface response plot respectively showing predicted the response of chromium (III) ion removal efficiency as a function of pH and contact time. The figure below shows as the effects of the independent variables and their mutual interaction on the removal efficiency of chromium (III) ion using MMOSP. The graph illustrated that as contact time increased at a lower level of pH and as pH value increases at the low level of contact time made a positive effect on chromium (III) removal

efficiency. Also, from figures, as contact time increase to the first 112.5 min removal efficiency chromium increases, and reach peak value beyond that removal efficiency decreases slowly. Also, as pH value increase 3 to around 5.5 the chromium removal efficiency increases and beyond that, it illustrates slightly decreases the removal efficiency, this indicates pH value of solution strongly affect the site of dissociation of the biomass surface and solution chemistry of the heavy metals. Generally, when contact time increase at lower of pH and when pH of the solution increases at lower contact time have positive effects on the efficiency of chromium (III) ion removal.

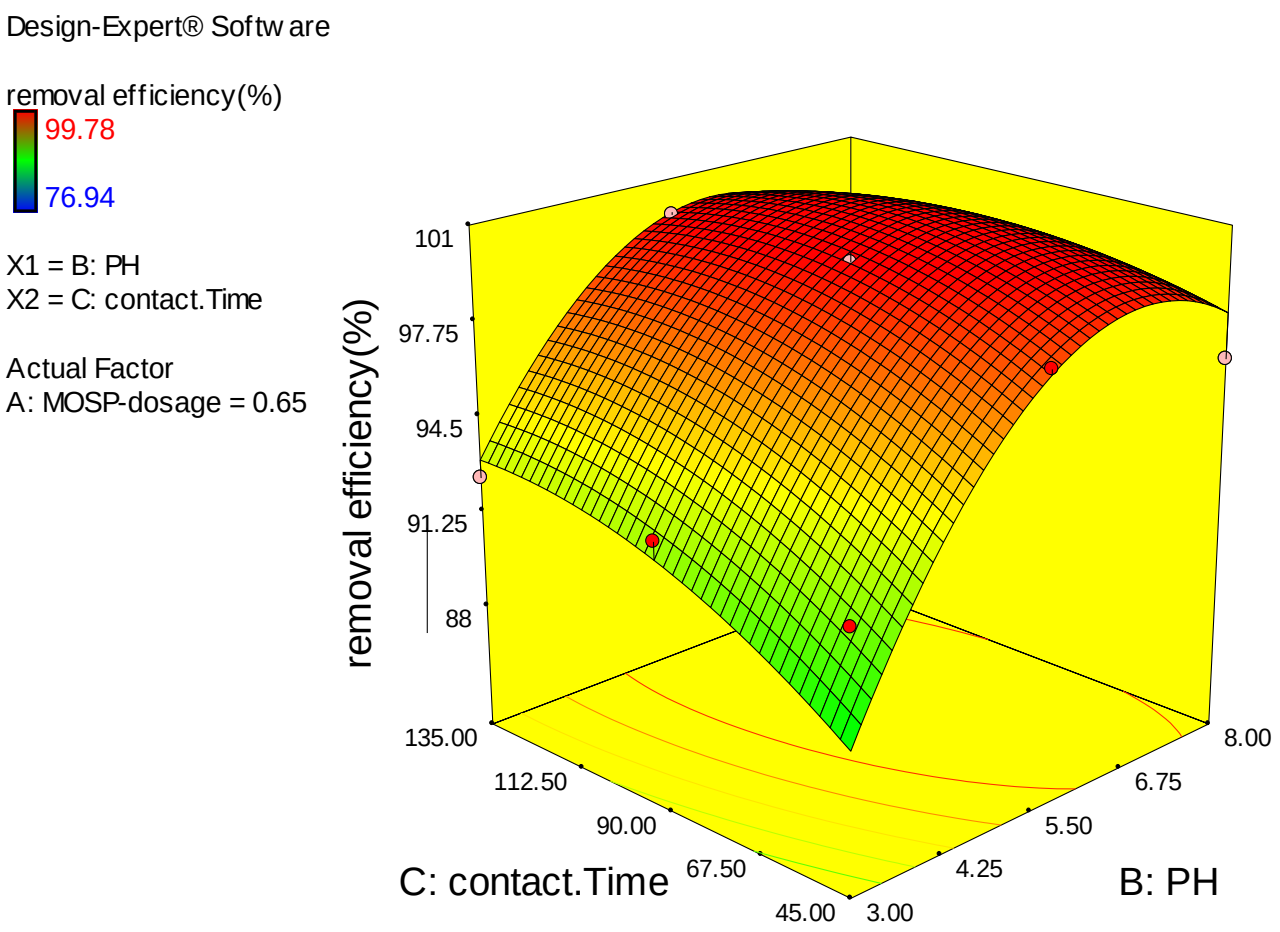

Figure 4.9: 3D plot of the effect of PH and contact time on Cr (III) removal efficiency

4.5. Evaluation of the adsorption isotherm models

Equilibrium isotherms model equations such as Langmuir and Freundlichare used to describe experimental adsorption data in the batch model to describe the relation between adsorbate on the surface of adsorbent that is the amount of species adsorbed per unit mass of adsorbent and concentration solute left in the solution (Gautam et al., 2014). The suitability of a certain adsorption isotherm to describe the obtained data depends on the correlation coefficient (R^2) of the profile representing the obtained data.

4.5.1. Langmuir Isotherm Model

The Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phases (Dada, 2015). The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. . This describes quantitatively the formation of a monolayer adsorb ate on the outer surface of the adsorbent, and after that, no further adsorption takes place. Based upon these assumptions, Langmuir derived in linear from represented:

$$\frac{Ce}{qe} = \frac{1}{KLqm} + \frac{Ce}{qm} \_\_\_\_\_ 4.4$$

Where, C_e, q_e, q_m and K_L representing the equilibrium concentration of chromium (III), adsorption capacity for MMOSP at equilibrium, the maximum capacity of MMOSP and Langmuir constant respectively. The q_m and R_L in the Langmuir isotherm can be determined by plotting (C_e/q_e) versus (C_e).The essential characteristics of Langmuir isotherm can be expressed by the dimensionless constant called equilibrium parameter R_L, equation 4.5:

$$\mathrm{RL} = \frac{1}{KLCo} \_\_\_\_\_ 4.5$$

Where C_o is the initial concentration of metal ion (mg/l), R_L is dimensionless equilibrium parameter. The characteristics of the R_L value indicate the nature of biosorption: - unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) and irreversible ($R_L = 0$) (Reddi et al., 2017).

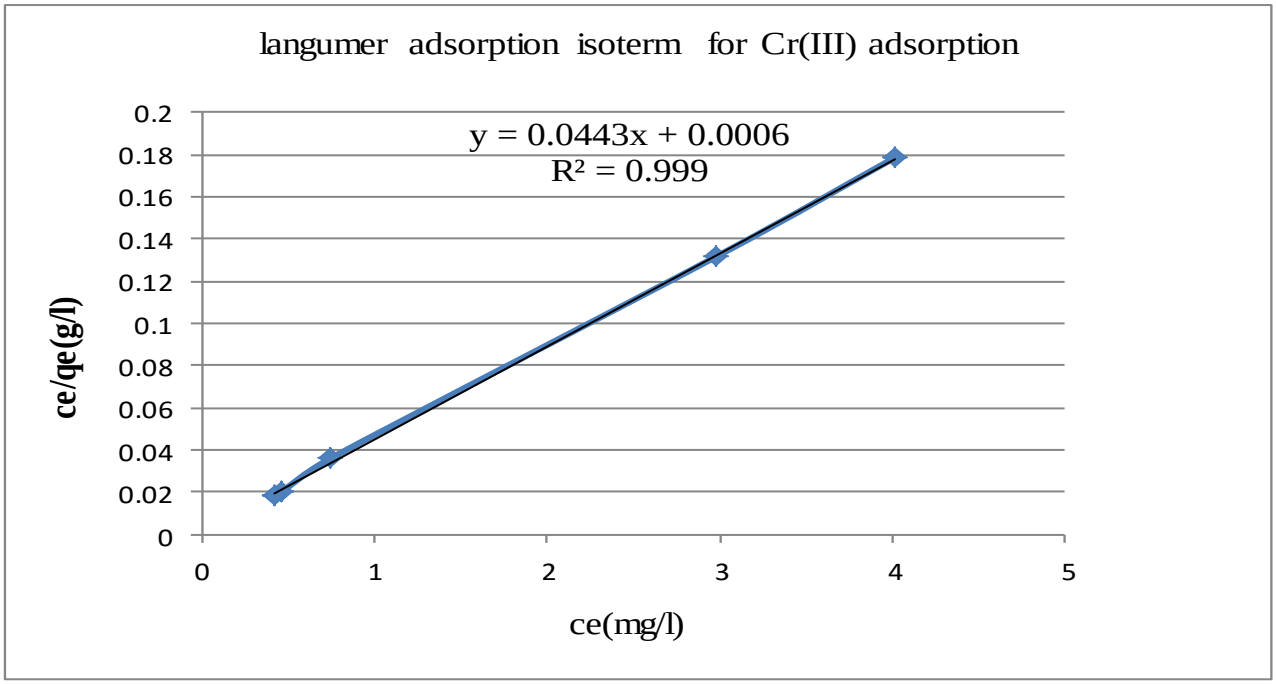

Figure 4.10: Langmuir isotherm model plot for Cr (III) adsorption at (Adsorbent dosage= 0.65g, pH=5.5, shaking and contact time 135min).

In this study, The RL values falls in between 0<RL<1which was calculated from Eq. (4.5). Therefore, the type of adsorption process of Cr (III) on to modified Moringaoleifera seedpod is favorable as shown in Table (4.6).

4.5.2. Freundlich isotherm model

The Freundlich isotherm model is describing the adsorption of solutes from an aqueous phase to a solid surface. The Freundlich isotherm model assumes that the uptake of metal ions occurs on a heterogeneous surface by multilayer adsorption and that the amount of adsorbate adsorbed increases infinitely with an increase in concentration. The Freundlich isotherm assumes several adsorption energies are involved in the adsorption process.Freundlich adsorption isotherm is the relationship between the amounts adsorbed per unit mass of adsorbent, qe, and the concentration of Cr (III) at equilibrium, Ce. The linear form of the logarithmic equation for Freundlich isotherm is written as equation 4.6 below.

$$\log qe = logkf + \frac{1}{nlogCe} \quad \text{4.6}$$

Where, K_f and n are the indicators of the adsorption capacity and adsorption intensity respectively. In this case, the plot of log C_e vs. log q_e was employed to generate the intercept value of K_f and the slope of =1/ n. Freundlich biosorption models for the removal of chromium (III) on the MMOSP was illustrated in figure 4.11.

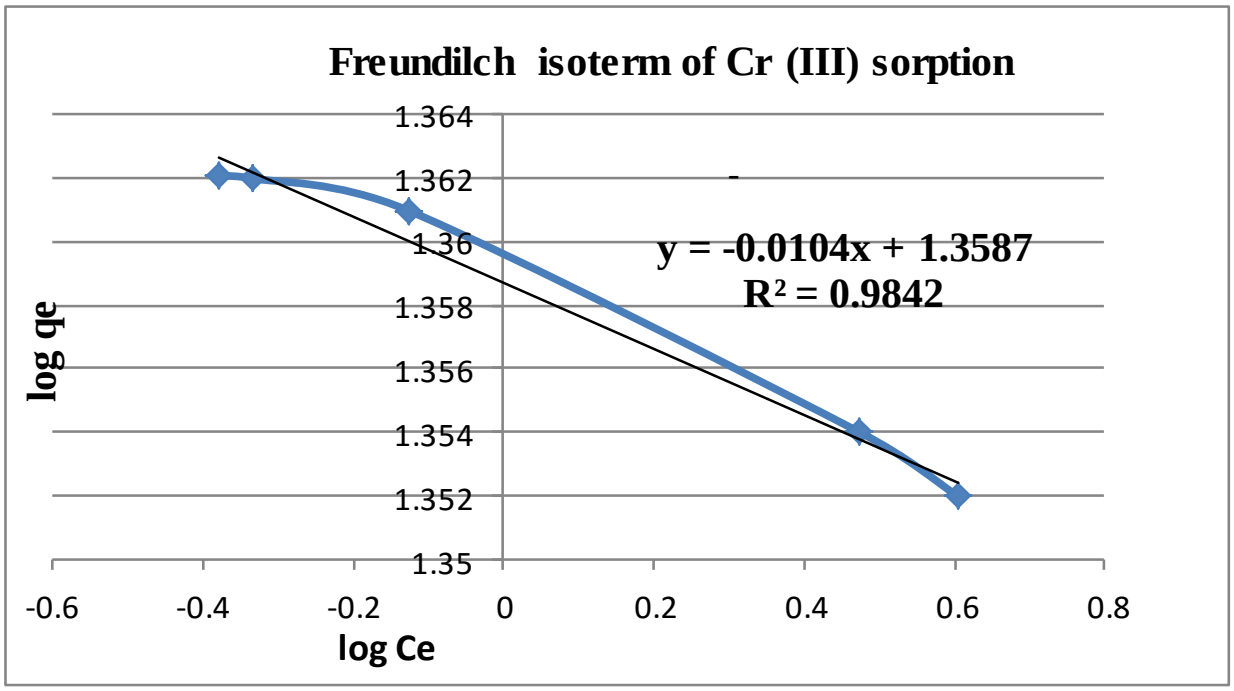

Figure 4.11: Freundlich isotherm model plot for Cr (III) adsorption (Adsorbent dosage= 0.65g, pH= 5.5 and contact time 135min).

Table 4.6: The Langmuir and Freundlich isotherm constants for the removal of Cr (III) using MMOSP.

Langmuir isotherm constants	Freundlich isotherm constants
q_{max}= 22.8733mg/g K_L= 73.8335L/mg R_L = 0.000090285 R^2=0.999	K_f =22.48mg/g 1/n=-0.0104 R^2= 0.984

Thus, the results implied that the regression coefficient (R^2) for Langmuir and Freundlich isotherms is made 0.999, and 0.984, respectively. Thus, from the result of correlation coefficient R^2 comparison of Langmuir and Freundlich isotherm models, the Langmuir adsorption isotherm is the fit model for chromium (III) ion adsorption onto the MMOSP. The Langmuir isotherm (R^2 = 0.999) fits the

experimental data very well, this describes that homogeneous distribution of active sites onto MMOSP adsorbent surface, since the Langmuir equation assumes that the surface is homogeneous. Form this study, obtain behavior of the adsorbent, Langmuir and Freundlich adsorption isotherms were plotted, and on the basis of the obtained correlation coefficients, it can be concluded that the adsorption of ions studied on prepared adsorbent given to the correlation coefficient higher than 0.999 follows Langmuir isotherm.

4.6. Adsorption Kinetics Model

Adsorption kinetic models correlate the adsorbate uptake rate with bulk concentration of the adsorbate. The pseudo-second-order equation is the most widely used kinetic models to describe the adsorption of a solute from a liquid solution. The pseudo-second-order equation fitted the adsorption data very well in a large quantity of literature reported (AL-Othman, 2012). Equally,large number of works has been reported where the second order kinetic model has been found to be the most suitable one for explaining adsorption of metal ions (Gupta, 2011). A relatively high R^2 value indicated that the model successfully describes the kinetics of metal adsorption. The kinetics of chromium (III) adsorption was studied from the time versus percentage of removal curves (mg/g). The figure 4.12 below describes the relationship time and amount of chromium adsorbed per MMOSP adsorbent (mg/g) which is used to analyze adsorption kinetics model.

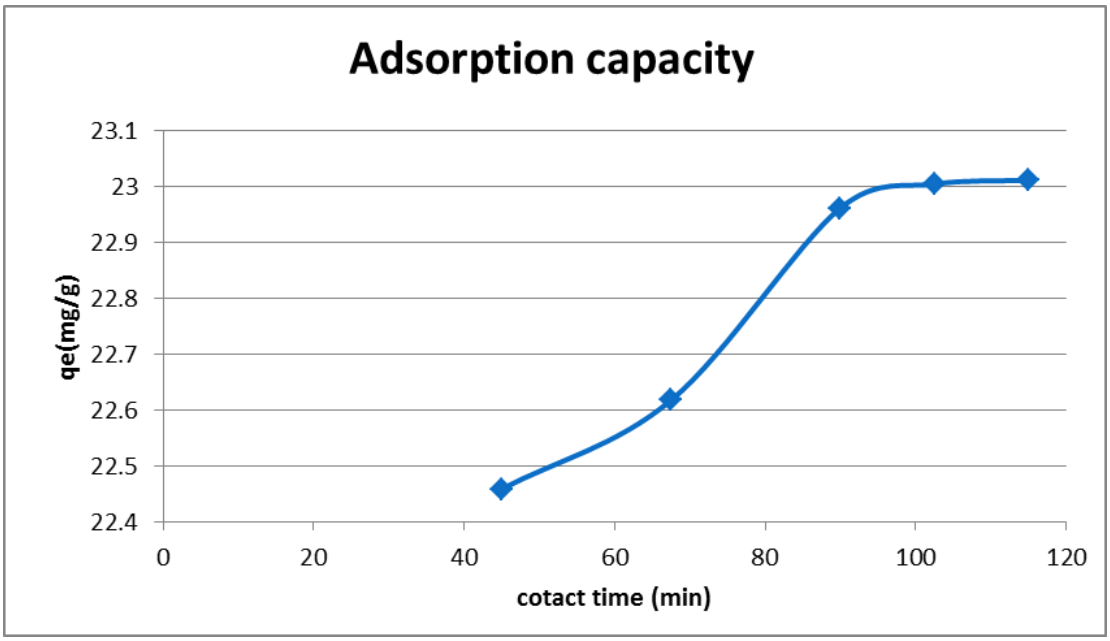

Figure 4.12: Adsorption capacity at (pH =5.5 adsorbent dosages= 0.65g, initial conc. =150mg/l, contact time varies from 45 min to 115min).

4.6.1. Pseudo-first-order Kinetic Model

In order to investigate the mechanism of adsorption, the pseudo-first-order equations were used to test experimental data of initial concentrations. The pseudo first order kinetic equation is represented blow:

$$\frac{dqt}{dt} = K1(\mathrm{qe} - \mathrm{qt}) \_\_\_\_\_ 4.8$$

Where, qe and qt are the adsorption capacities at equilibrium and time t respectively (mg/g) and k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}). The equation can be rearranged into:

$$\log(\mathrm{qe} - \mathrm{qt}) = logqe - \left(\frac{K1}{2.303}\right)t \_\_\_\_\_ 4.9$$

The values of log (qe - qt) were linearly correlated with t. The plot of log (qe - qt) vs. t should give a linear relationship. The first-order rate constant k_1 (1/min) and the equilibrium capacity qe can be obtained from the slope and intercept, respectively. The observed rate constant for the removal of Cr (III) ions using MMOSP for this Pseudo-first-order kinetic model was described in figure 4.13below.

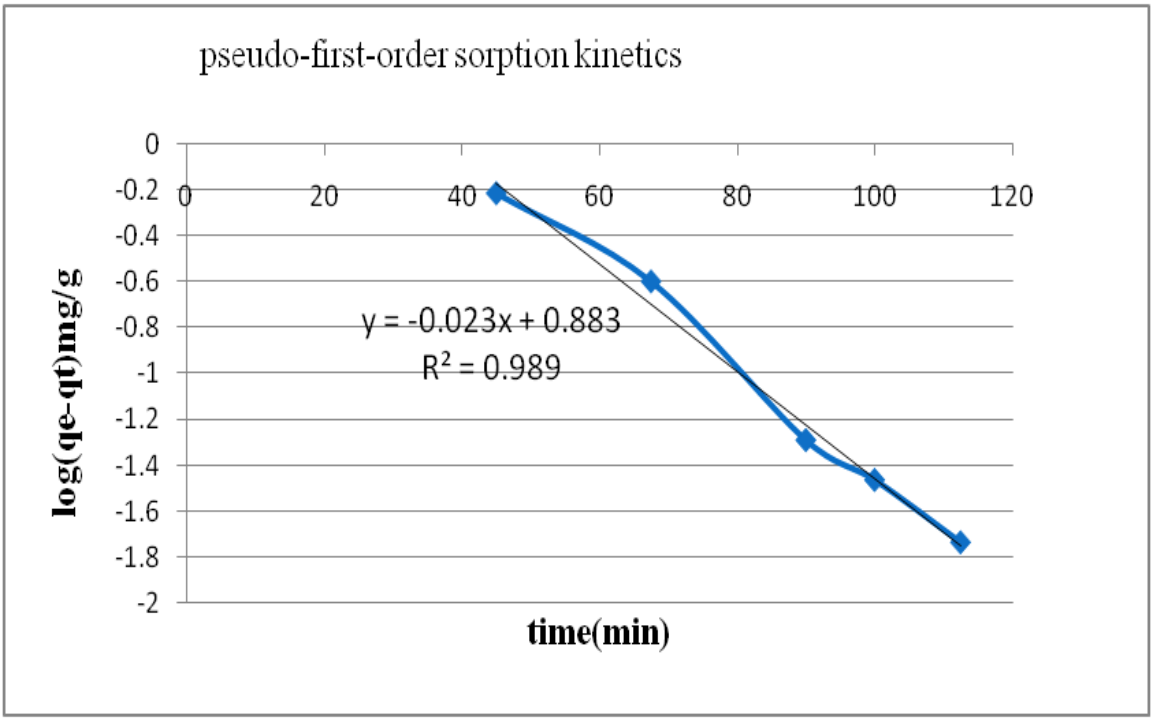

Figure 4.13: Pseudo -first-order kinetic model plot Cr (III) adsorption. (Adsorbent dosage=0.65g, initial concentration =150mg/l, pH= 5.5 and with contact time 45 to 115 min).

4.6.2. Pseudo-second-order Kinetic Model

In this investigation, pseudo-second-order used to analyze the kinetic process of chromium (III) ion adsorption onto MMOSP. The pseudo-second-order adsorption kinetic is expressed as in equation bellow

$$\frac{t}{qt} = \frac{1}{K2qe^2} + \frac{t}{qe} \quad \text{4.10}$$

Where qe and qt are the sorption capacity at equilibrium and time t (mg/g), respectively, k_2 is the rate constant of the pseudo-second-order sorption (g/mg min). The k_2 and qe are found from the intercept and slope of t/qt versus t linear plot such that qe = 1/slope and k_2 = slope^2/intercept. (Admasu, 2016)

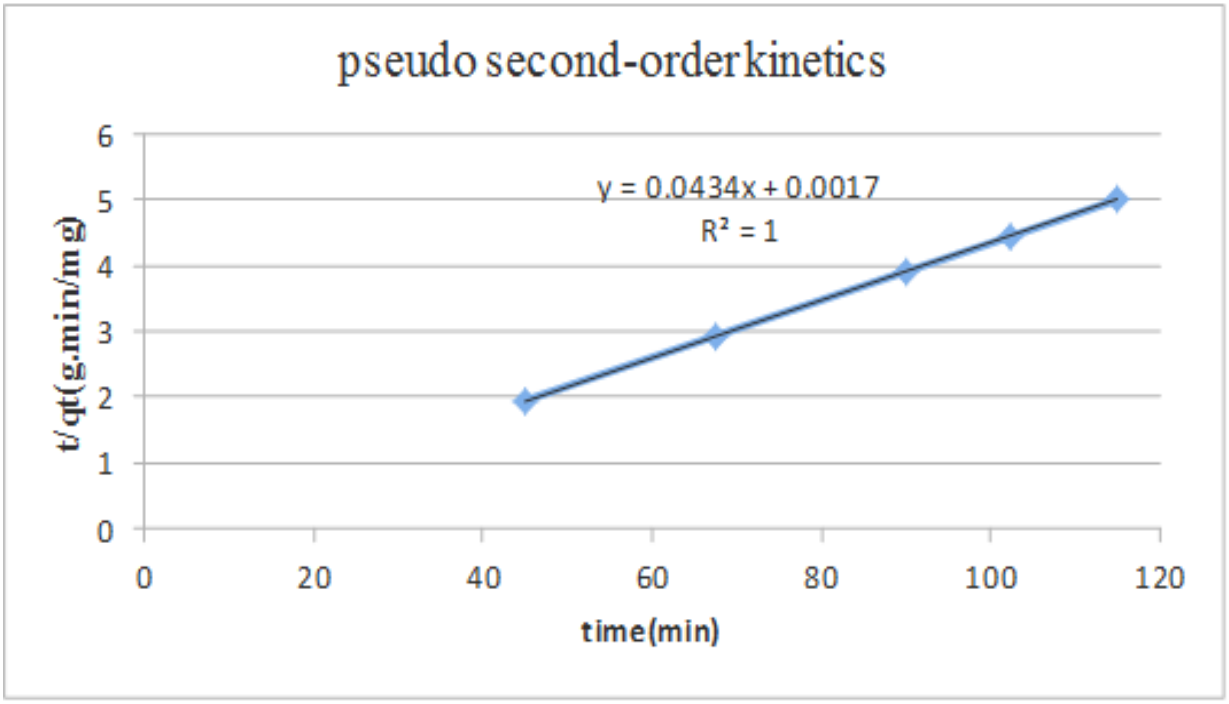

Figure 4.14: Pseudo second-order kinetic model plot Cr (III) adsorption (Adsorbent dosage=0.65g, initial concentration = 150mg/L, pH=5.5 with contact time 45 to 115 min).

The above results demonstrated that, Pseudo second-order kinetic equations have high R^2 (R^2= 1) Therefore, from the above figure 4.14, concluded that the sorption of chromium (III) ions from tannery wastewater using MMOSP were found to follow Pseudo second-order kinetics equations.

Table 4.7: Adsorption kinetic model parameters of Cr (III) on the MMOSP.

First Order Kinetic Parameters	Second Order Kinetic Parameters
q_e (mg/g) (cal)=7.64 $K_1(min^{-1})$=0.053 R^2=0.989	q_e(mg/g)(cal)= 23.041 q_e (mg/g)(exp)=23.012 $K_2(g.mg^{-1}.min^{-1})$ =0.0481 R^2=1

The result observed that in Table 4.7, Pseudo second-order kinetic equations have high R^2 (R^2= 1) values and sorption capacity qe (mg/g), calculated and experimental value near to same value. Therefore, a Pseudo second-order kinetics model was taken as the fit equations for the description of the mechanism of sorption of chromium (III) ion using MMOSP. Therefore, from the table concluded that the sorption of chromium (III) ions from model pollutants onto MMOSP was found to follow Pseudo second-order kinetics equations.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusion

The *Moringa oleifera* found in semi desert part Ethiopian, the leave and seed are used for different purpose including wastewater treatment, but the seedpod as newly alternative adsorbent for Cr (III) removal was investigated by making simple modifications with methanol and nitric acid to increase the

Percentage of removal efficiency of chromium from aqueous solution using batch adsorption techniques the results indicates that the modified *Moringaoleifera* seedpod is a good adsorbent.

In order to know the potential of *moringaoleifera* seedpod for removing Cr (III) from aqueous solution, the experiments was conducted with varying adsorbent dosage, pH, and contact time at constant initial model pollutant concentration, shaking speed and at room temperature. The result indicates that the modified *moringaoleifera* seedpod is having the potential to removal Cr (III) from model pollutant. Thus, Cr (III) removal using MMOSP reached 99.78% at adsorbent dosage 0.65g, pH 5.5, and contact time at 90min. In addition, the adsorption Cr (III) highly dependent on pH and contact time, which are significant factor, it indicates as pH and contact time increases the removal efficiency increases until equilibrium.

The FTIR analysis describes that the adsorbent *moringaoleifera* seedpod contain functional groups such as the presence of phenol groups of cellulose and lignin, alkynes' group and aliphatic structures and alcoholic group respectively. Those functional groups participate on chromium binding on to surface of *Moringa oleifera* seedpod and the X-ray Diffraction analysis indicates that MOSP have properties of highly an amorphous.

The adsorption kinetics studies indicated at equilibrium in the adsorption of Cr (III) ion was reached in 115min of contact between the MMOSP and the solution. It was found that the kinetics of the adsorption on *Moringa oleifera* seedpod followed by pseudo-second-order. The Langmuir and Freundlich theories were used to describe the distribution chromium ion in between the solid and liquid and the Langmuir isotherms showed a better fit to the process (R^2= 0.999).

This study shows as the modified *moringa oleifera* seedpods have a better removal efficiency of chromium (III) from model wastewater.

5.2. Recommendation

From this study work, we understand the modified *Moring aoleifera* seedpod have an ability to remove chromium (III) from aqueous solution, therefore, the following direction of work is recommended to use in real tannery wastewater treatments.

In this study, show as only the effect of adsorbent dosage, pH, and contact time. However, other parameters are not included so, it needs further study to increase the efficiency of chromium (III) ion uptake from real pollutants.

It is recommended to conduct a research on other toxic industrial wastes such as dyes and other metals to evaluate the efficiency of *Moringa oleifera* seedpod.

Optimize the removal efficiency of the modified *Moringa olifera* seedpod adsorbent through continuous column experiment, and try to immobilize the adsorbent on materials to improve its removal capacity.

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APPENDICES

Appendixes I: Proximate analysis of raw MOSP & MMOSP

Moisture content

Weight of sample taken for all is 2g

$$Mc = \mathbf{100} \times \frac{\boldsymbol{wi - wf}}{\boldsymbol{wi}} \_\_\_\_\_ 1$$

Moisture content of MOSP

For MOSP $Mc = 2g - \frac{1.896g}{2g} \times 100 = 5.2\%$

For MMOSP $Mc = 2g - \frac{1.916}{2} g \times 100 = 4.21\%$

Where,

Mc= Moisture content

Wi= Initial weight MOSP/MMOSP

Wf = after drying MOSP/MMOSP

Ash Content of MOSP

$Ac\ \%) = \frac{Wa}{Wf} x\ 100\% \_\_\_\_\_$ (2)

For MOSP $Ac = \frac{1.3}{2} x\ 100 = 35\%$

For MMOSP $Ac = \frac{1.55}{2} x\ 100 = 27.2\%$

Where,

Wa=weight of ash MOSP/MMOSP

Wf=original weight of MOSP/MMOSP

Volatile Content

$Vc(\%) = \frac{(Wi - Wf)}{Wi} x\ 100\ \% \_\_\_\_\_$ (3)

For MOSP $Vc = \frac{(2-1.2006)}{2} x100 = 39.97\%$

For MMOSP $Vc = \frac{(2-1.356)}{2} x100 = 32.2\%$

Where;

Vc=volatile component in percentage

Wi =the original weight of MOSP/MMOSP

Wf=the weight of MOSP/MMOSP after cooling

Fixed Carbon

$Fc\ (\%) = 100 - Vc - Ac - Mc$ _____(4)

For MOSP $Fc = 100 - 35 - 39.97 - 5.2 = 19.83\ \%$

For MMOSP $Fc = 100 - 27.2 - 32.2 - 4.2 = 36.6\%$

Where,

VC=volatile content

Ac=ash content

Mc= moisture content

Bulk Density (Bd)

$Bulk\ Density\ (BD) = \frac{Ms}{Vs}$ _____ (5)

For MOSP $Bd = \frac{2}{1.1997} cm3 = 1.667\ g/cm3$

For MMOSP $Bd = \frac{2g}{1.6} cm3 \frac{2}{1.6} cm3 = 1.25\ g/cm3$

Where,

S=mass of MOSP/MMOSP

Vs= volume ofwater displaced (cm^3)

Appendix II: design (actual) @design expert 7.0

RUN	A-MOSP dosage(g)	B-PH	C-cont. Time(min)	Removal efficiency (%)
1	0.3	3	45	76.94
2	0.65	3	45	92.38
3	1	3	45	90.37
4	0.3	5.5	45	89.84
5	0.65	5.5	45	98.17
6	1	5.5	45	96.32
7	0.3	8	45	93.32
8	0.65	8	45	96.56
9	1	8	45	96.83
10	0.3	3	90	83.97
11	0.65	3	90	92.63
12	1	3	90	88.18
13	0.3	5.5	90	97.29
14	0.65	5.5	90	99.78
15	1	5.5	90	99.16
16	0.3	8	90	96.41
17	0.65	8	90	97.9
18	1	8	90	94.78
19	0.3	3	135	90.31
20	0.65	3	135	92.49
21	1	3	135	90.57
22	0.3	5.5	135	96.31
23	0.65	5.5	135	99.74
24	1	5.5	135	94.27
25	0.3	8	135	94.1
26	0.65	8	135	96.08
27	1	8	135	93.48